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Reorganization of the organic chapter in chemistry for secondary school textbooks

# BOSTON UNIVERSITY SCHOOL OF EDUCATION

Thesis
Quallins, G.A.
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## BOSTON UNIVERSITY

## SCHOOL OF EDUCATION

Thesis

THE REORGANIZATION OF THE ORGANIC CHAPTER IN CHEMISTRY FOR SECONDARY SCHOOL TEXT-BOOKS.

Submitted by

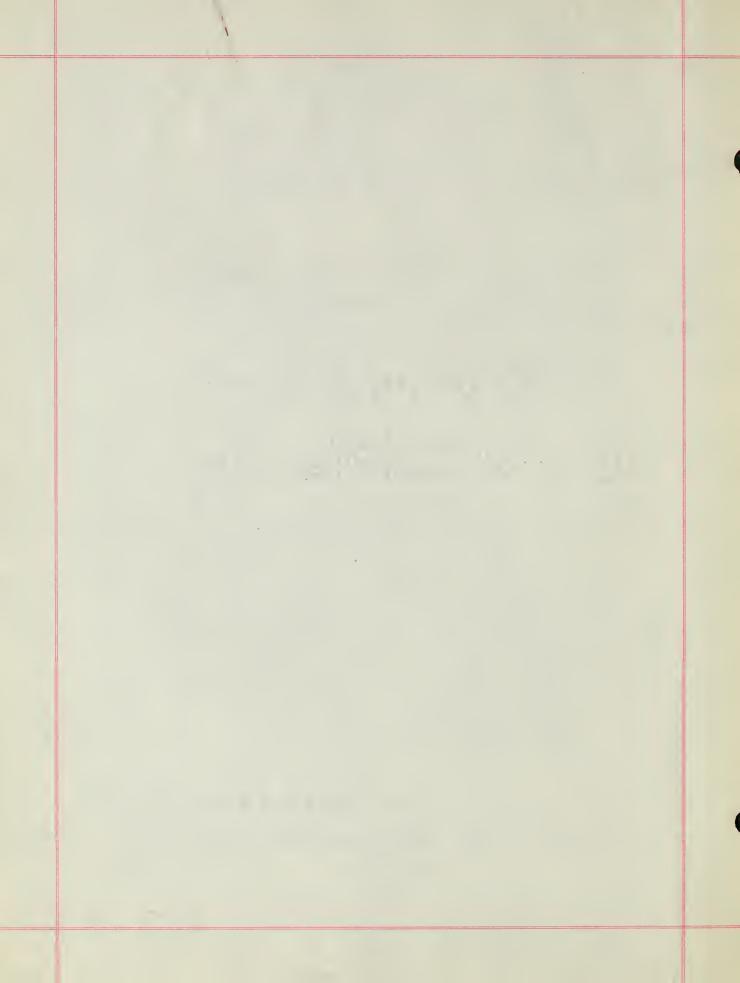
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(B.S. in Electrical Engineering, Georgia School of Technology, 1923.)

In partial fulfillment of requirements for the degree of Master of Education.

1933.

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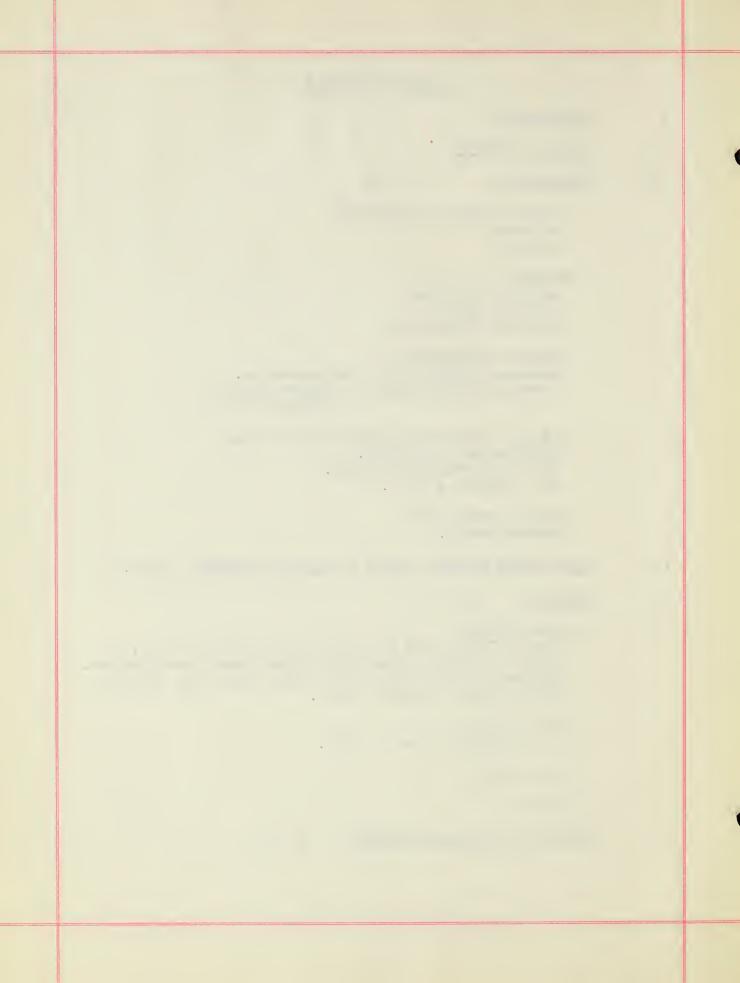
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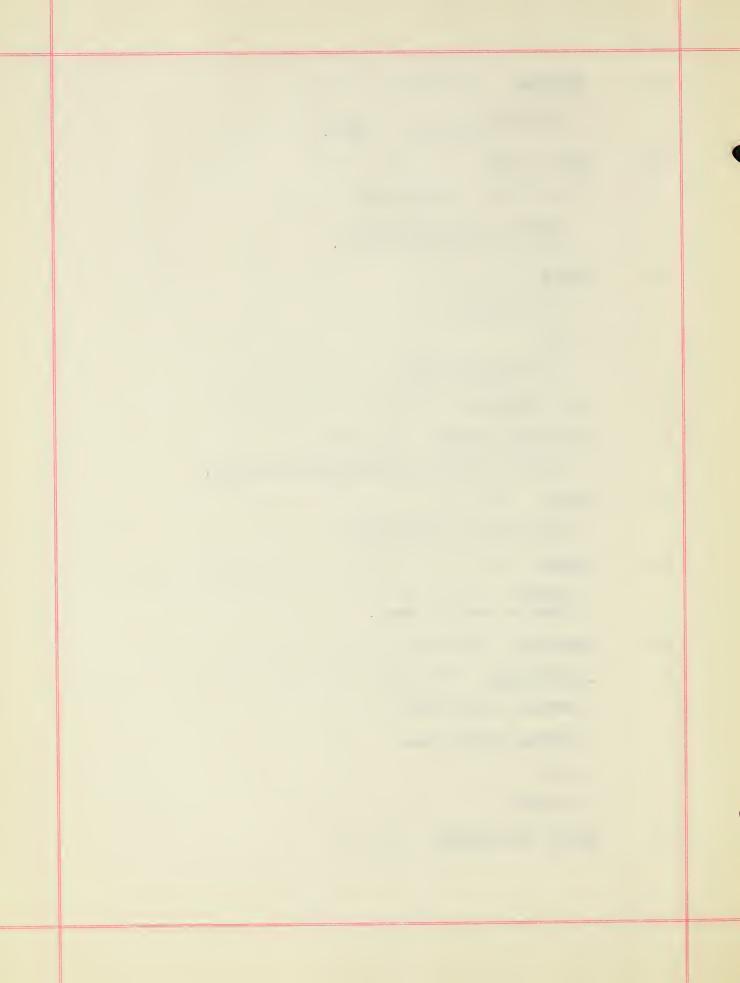
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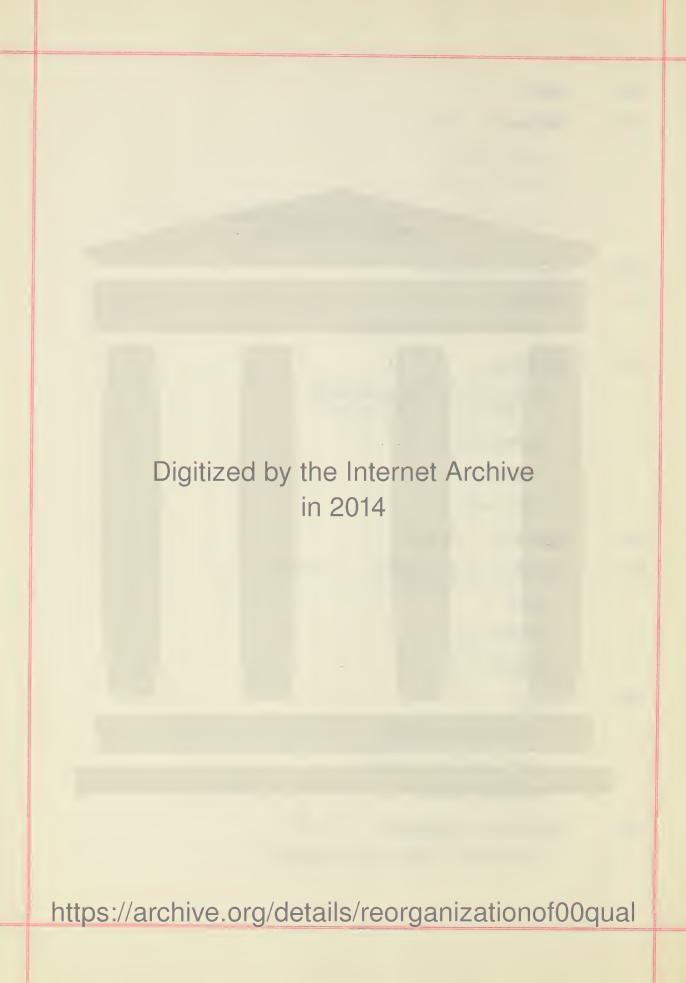
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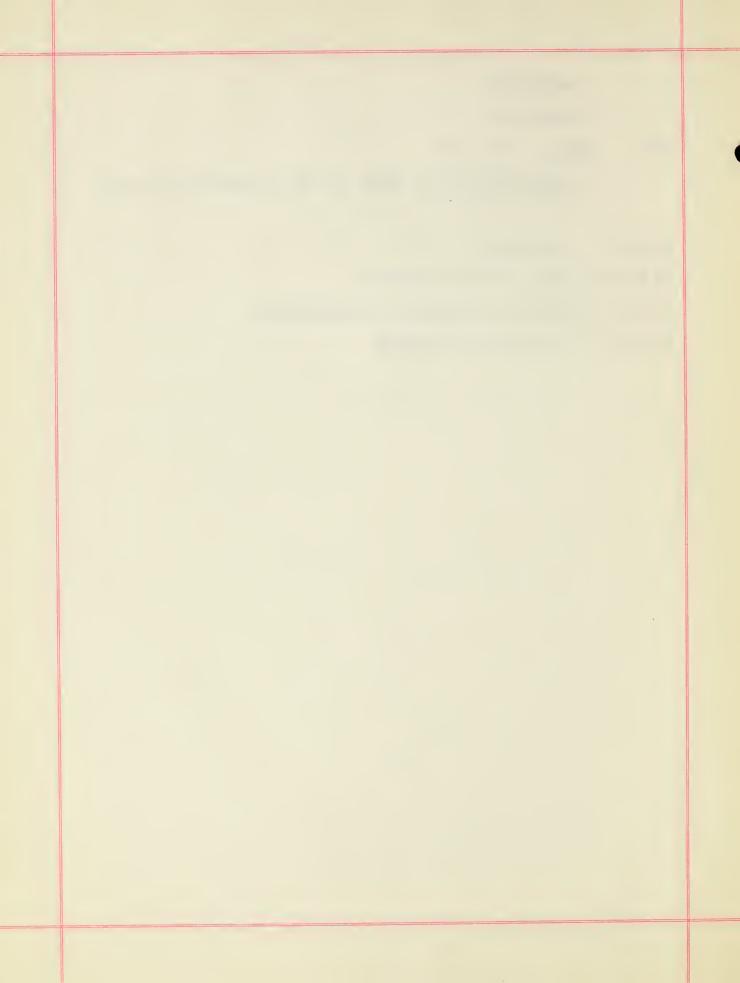
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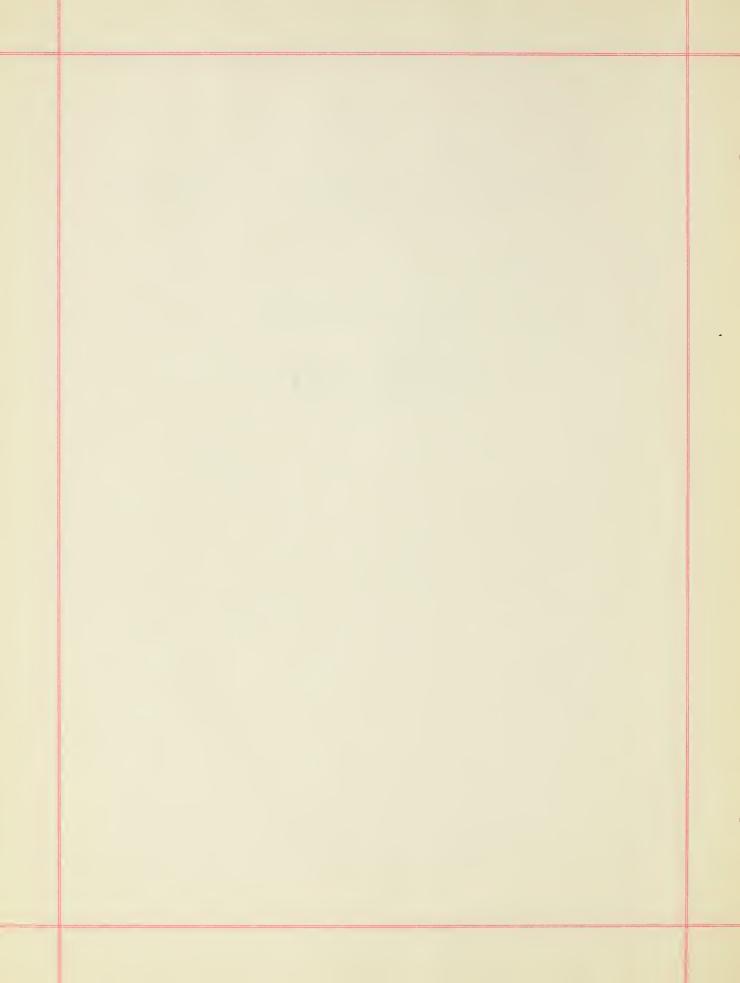
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INTRODUCTION



## INTRODUCTION

The purpose of this thesis is to review the content of the organic chapter in high school chemistry text-books and present material which represents the choice of a certain number of teachers together with the results of my own studies and experience regarding the kind and amount of material which should be incorporated as the organic part of a high school course in chemistry.

A questionnaire was sent out. The results are incorporated in the thesis and also systematically summarized in appendix III.

The acquisition of a basic knowledge of organic chemistry is facilitated by a study of the structure of a compound. As a matter of fact organic chemistry is to a large extent structural chemistry. The structural formulas reveal the inner nature of the things they represent, and a knowledge of them is necessary for the understanding of the various classifications in organic chemistry. The study of structural formulas and the theoretical phase of organic chemistry has not been neglected in the attempt to introduce the chemistry of the every-day-materials with which the student comes in contact.

The production and uses of common materials which come under our daily observations are rapidly increasing from year to year. This production of new material (mostly organic)

-- II . 1 1 4 

changing times constant revision is necessary accompanied by the continual introduction of new material. New material makes the course more interesting to both the instructor and the student. In this compilation use has been made of suggestions which have been received from all parts of the United States.

Since time does not always permit the study of the organic chapter in detail in a one year general chemistry course, the material selected from that chapter for study depends upon the judgement of the instructor and will vary with the type of class under instruction. In this treatise an attempt has been made to introduce enough of a variety of material suitable for any class which might come under the instruction of a chemistry teacher.

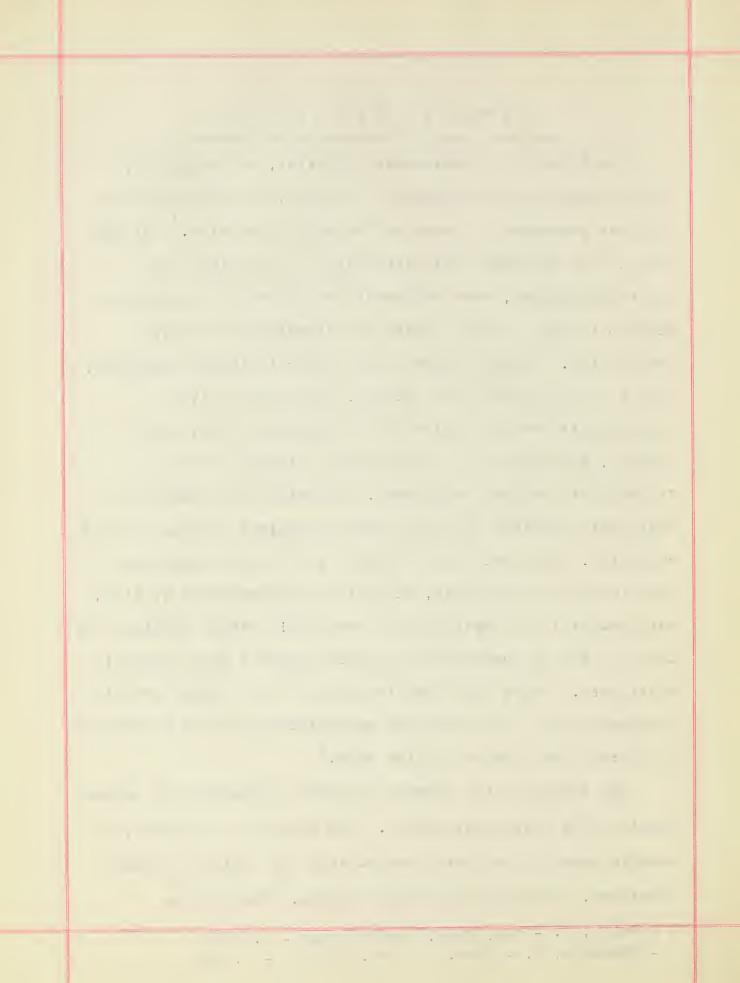
## ORGANIC CHEMISTRY

The majority of substances composing, or produced by living organisms are compounds of carbon, and the chemistry or these compounds is known as "organic" chemistry. At one time it was believed that substances of the animal and vegetable kingdom, were different from those of the mineral kingdom in that a "life force" was necessary for their preparation. Since bodies of the mineral kingdom apparently show no motion caused from within, and are not living organisms as are the bodies of the animal and vegetable kingdom, the chemistry of the mineral kingdom is called "inorganic" (without organisms). Likewise the chemistry of substances obtained from all living organisms has been called "organic". The artificial production of organic compounds from inorganic substances, without the intervention of life, was thought to be impossible at one time! Wohler refuted this idea in 1828 by preparing an organic compound from inorganic substances. Since that time the number of so called organic compounds which have been made synthetically in the laboratory has passed the quarter million mark.

The boundary line between inorganic chemistry and organic chemistry is rather indistinct. The metallic carbonated, for example usually are considered outside the realm of organic chemistry, although they contain carbon. There is no

<sup>1 -</sup> Smith, A. - Gen. Chem. for Colleges - p. 375

<sup>2 -</sup> Dinsmore, E. - Chem. for Sec. Schools - P. 325



scientific reason today for the distinction between organic and inorganic compounds. But partly for convenience (educationally) and also from habit, these classifications still exist.

The great number of carbon compounds in existence is explained by the fact that the valence of carbon is four, and its atoms have the ability to combine with each other in chains or rings. The hydrocarbons illustrate, in a spectacular way, the manner in which carbon atoms may be linked together.

## HYDROCARBONS

Hydrocarbons may be classified as follows:-

- (1) "The <u>aliphatic</u> or 'chain' compounds in which the carbon atoms in each molecule are arranged in straight or branched chains."
- (2) "The aromatic compounds in which the molecular structure contains one or more closed chains or rings of carbon atoms. These were called aromatic because some of the first known members of this group possessed pleasant aromatic odors."

The following page contains examples of aliphatic and aromatic compounds. The structural formula is used to show how the carbon atoms can combine with other carbon atoms to form "rings" or "chains".

<sup>3</sup> Chem. Warfare School, Book II - Chem. Warfare Agents - P. 71

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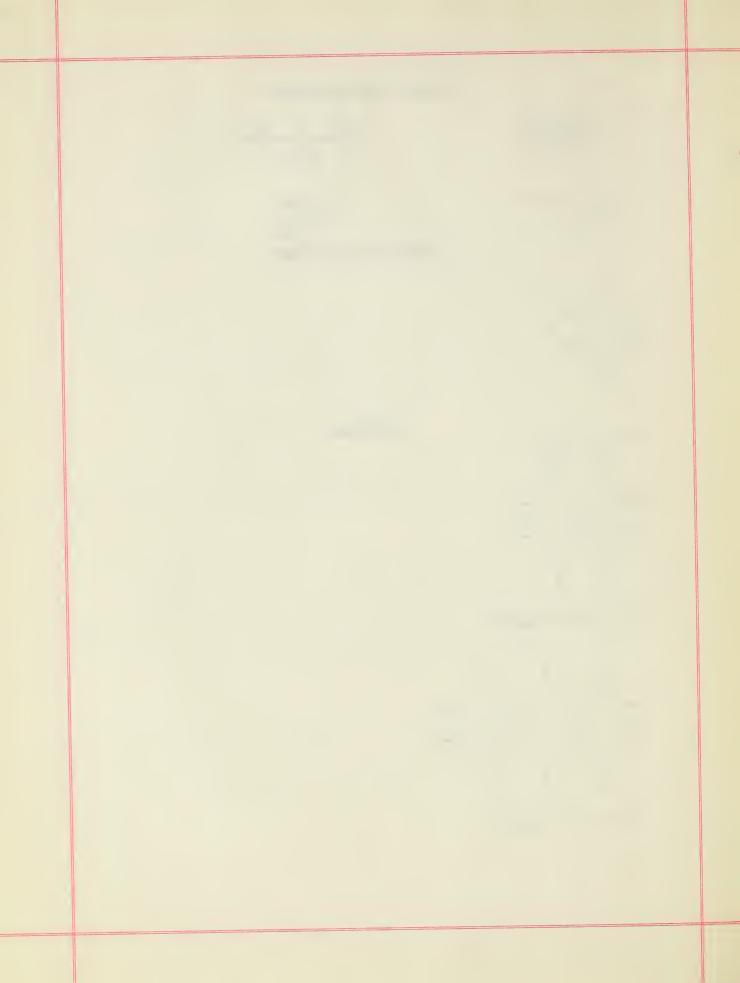
# Aliphatic Hydrocarbons

# Aromatic Hydrocarbons

# FIGURE A

Maphthalene (C<sub>10</sub>H<sub>8</sub>)

Anthracene (C<sub>14</sub>H<sub>10</sub>)



The consideration of petroleum belongs with our study of the hydrocarbons for petroleum is a complicated mixture of hydrocarbons composed very largely of those of the methane series having the general formula  $C_nH_{2n}+_2$  and the members from C  $H_4$  to  $C_{35}H_{72}$  have been isolated from it. It seems best to present the subject at this time just before taking up the study of the first series of hydrocarbons inasmuch as the most important problems in connection with petroleum will be solved by means of the chemistry of this series.

## PETROLEUM

Petroleum is a more or less viscuous, oily, inflammable fluid with a distinctive odor. When the substance contains sulphur, as is often the case, the odor is rather disagreeable. Its fluidity is dependent upon its temperature as well as its composition. The color varies from white to brownish or black when viewed by transmitted light and is usually greenish by reflected light.

Composition - Petroleum is composed essentially of hydrogen and carbon combined as various hydrocarbons. Although samples from various oil fields vary greatly in composition, all of them contain hydrocarbons of the methane series and are complex mixtures.

# Origin of Petroleum

The following two theories have been supported in regard

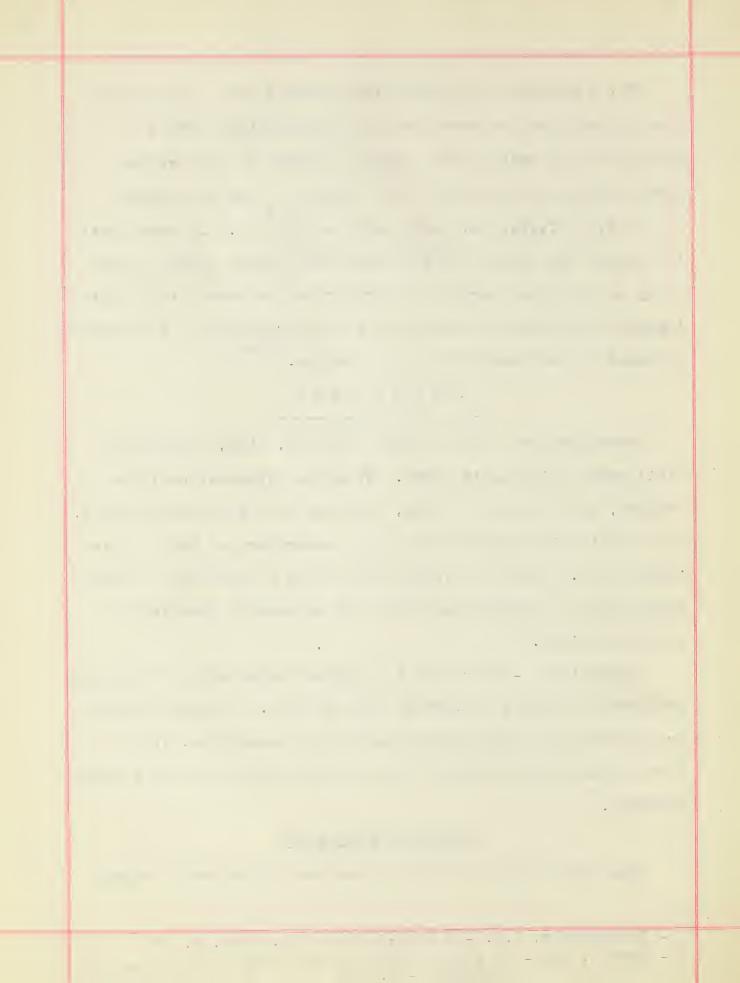
<sup>4 -</sup> Chamberlain, J.S. - A Text-book of Org. Chem. P. 37

s - Remson, Ira - An Introduction to the Study of the compounds

of Carbon - P. 117

- Butler, G. M. + Tenney, J. B. - Univ. of Arizona Bulletin-P.P. 5-7

- Williams, R. J. - An Introduction to Ora. Chem. - P. 27



to the origin of oil:-

The inorganic theory: - Those who support the inorganic theory claim that petroleum has been formed by a chemical reaction between superheated steam and metallic carbides deep below the surface of the earth. The opponents of the inorganic theory point out that deposits of petroleum have such rock associates as would lead one to doubt very much that the oil had originated in the manner suggested.

The organic theory: - According to the organic theory, petroleum has originated by a process of natural distillation of the remains of sea organisms - both plant and animal, which settled on the bottom of the sea and were subsequently covered with layers of mud. Enormous thicknesses of such sediment thus accumulated, and by cementation and pressure the sediments were changed into shale and rock strata. By certain chemical processes the organic material was converted into petroleum. The asphalt-base oils are believed by some to have been formed from animal matter and the paraffin-base oils from plant organisms. There is a vast store of evidence of the correctness of this theory and few question it.

# Drilling for oil

Sub-surface water tends to push oil upward on account of the oil being lighter. When the oil in rising encounters some impervious layer like clay or shale existing as an inverted trough, the oil is trapped beneath the clay or shale. (see

<sup>6 -</sup> Butler, G. M. and Tenney, J. B. - Univ. of Arizona Bulletin P. 7-8

,  figure 1, page 7) In order to tap these reservoirs we have to drill through to the oil pocket.

There are two types of drilling systems in use, the standard method which operates on the principle of percussion, and the rotary system which operates on the principle of torsional grinding.

With the standard method of drilling use is made of a heavy stem and bit, alternately raised and dropped on the bottom of the hole, thus pulverizing the rock strata by percussion.

The principle of the rotary system of drilling is the use of torsional grinding, similar to an augur, with a fluid circulation to wash the cuttings from the bottom of the hole to the surface.

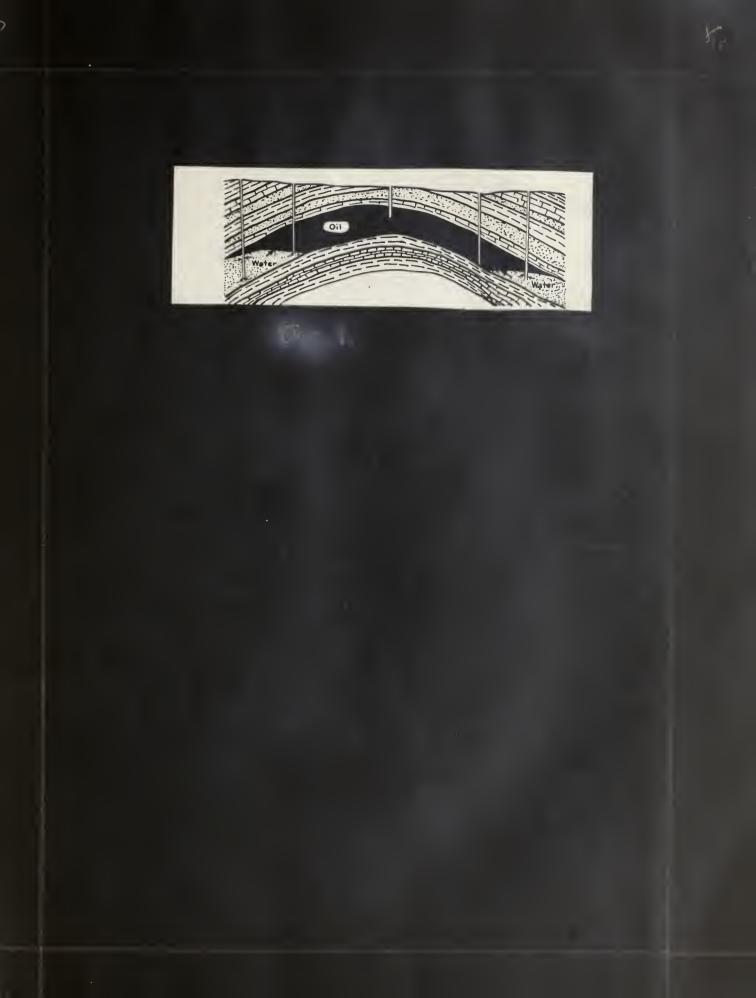
Advantages of the standard system: -

- l. Less initial cost of tools and rigging.
- 2. Less labor cost per day.
- 3. Less cost per foot for shallow depths.
- 4. Less power required.

Disadvantages of the standard system:-

- l. Longer drilling time.
- 2. Greater cost per foot for deeper holes.

----





Advantages of the rotary system: -

- 1. Faster drilling.
- 2. Less trouble from caving formations.
- 3. Less cost per foot for deeper wells.

Disadvantages of the rotary system: -

- 1. Greater daily labor cost.
- 2. Greater cost per foot for shallow holes.
- 3. Greater power consumption.

The circulatory system: It is necessary to use a circulatory system when drilling in sandy formations to keep the casing free and remove cavings and cuttings. By setting up pumps with hose connections to a circulatory head on the casing through which the drilling line works in a stuffing box, mud fluid can be circulated down the inside of the casing and up the outside as drilling goes on. This removes all sand and leaves a mud wall between the casing and the sandy formation.

The exclusion of water: - Water can do great damage to an oil field if allowed to flow down to the oil between the wall of the well and the casing. To prevent this, below each layer of water sand, the space between the well wall and the casing is filled with cement (see Figure 2). This process is called "cementing off" the water. The cement must be satisfactory for this work and to insure this, it must pass certain specifications. One method of cementing off is as follows: - The casing is raised one joint off bottom and circulation established. The

<sup>8 -</sup> Phelps, R. W. and Lake, F. W. - Petroleum Engineering - Pp. 199 - 221

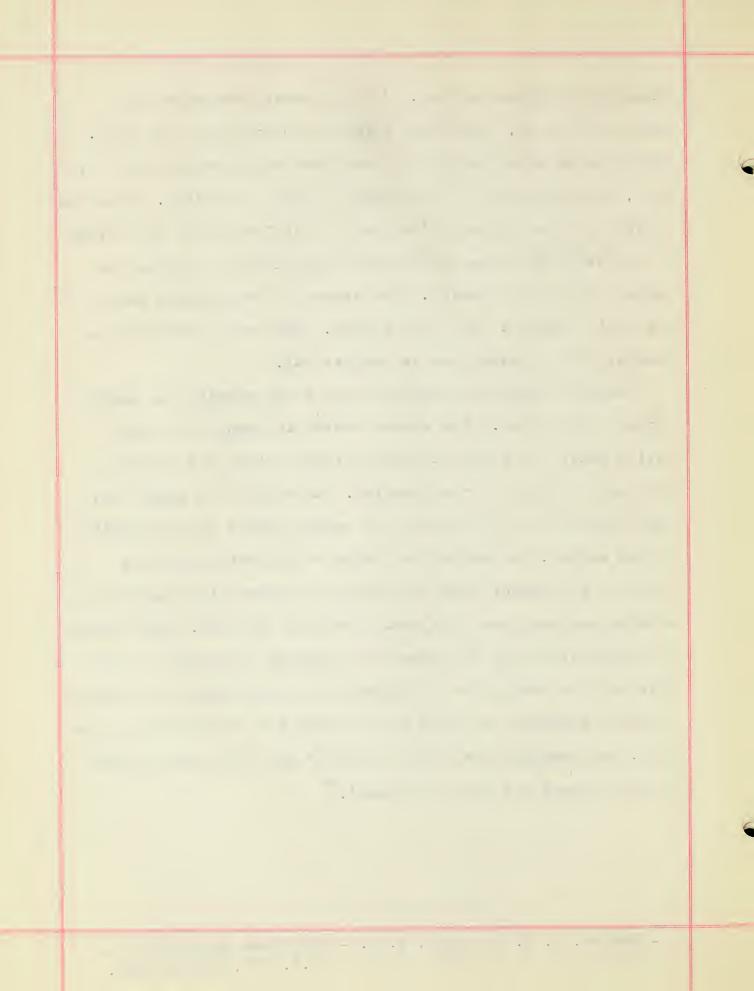
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pumps are disconnected and, with the casing suspended one joint off bottom, the cement mortar is lowered into the hole.

After the required amount of cement has been lowered into the hole, the top joint of the casing is again connected. When the casing has been properly "sealed", it is lowered to the bottom of the well and causes sufficient displacement to force the cement back of the casing. The cement is thus sealed back of the casing until it has time to set. The small amount which remains in the casing can be drilled out.

Another method of cementing off is by pumping the cement through the casing. The cement mortar is pumped down the inside while the casing is being slowly raised and lowered a few feet to keep it from freezing. After all the cement has been pumped to the bottom of the casing and is on the outside of the casing, the casing is landed on the bottom and the gates in the cement head are closed to prevent the cement from circulating back into the casing until it has set. One method of determining when the cement has reached the bottom of the hole and the casing can be landed is by calculating the amount of water necessary to displace the cement to the bottom of the hole, and pumping this amount of water into the casing after all the cement has been introduced.

<sup>8 -</sup> Phelps, R. W. and Lake, F. W. - Petroleum Engineering - P.P. 203, 223 and 224.



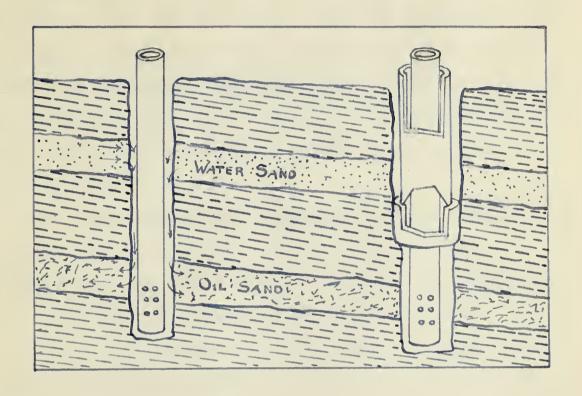
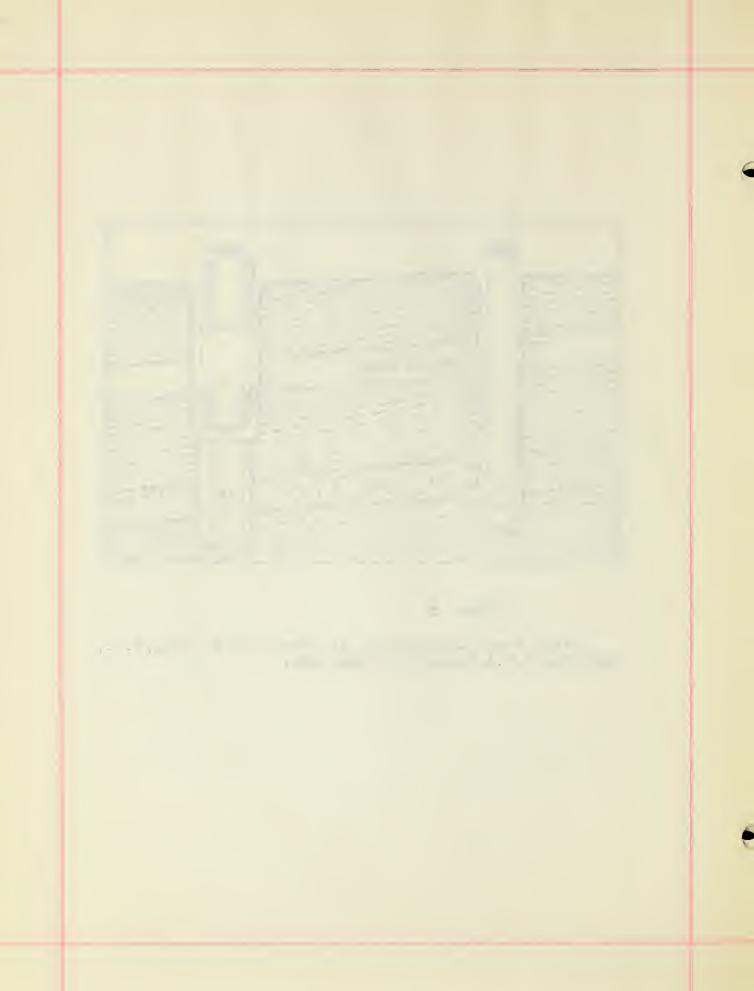


FIGURE 2

Taken from Fundamentals of Chemistry by Gray, C.W., Sandifur, C.W.& Hanna, H.J. Page 480.



Refining of petroleum: - The refining of petroleum consists of first, the removal of water and second, distillation.

crude oil usually contains a considerable amount of water emulsified in the oil and before it can be distilled it is necessary to remove the water. The emulsion is "broken" by passing the crude petroleum between two plates having a high potential difference. This causes the minute particles of water to collect in drops which settle out and are thus separated from the oil.

The various hydrocarbon compounds contained in petroleum have different boiling points and densities and can be separated from each other by distillation. One method of distillation which is in common use is as follows:

The crude oil is distilled in a series of horizontal cylindrical stills, connected to distil continuously. Figure 2, page 10 shows the principle on which this method works. "The crude oil pumped in at a determined rate increases in temperature as it passes from one distillate heater to another as the result of cooling the vapors from the stills, which travel through the coils on their way to the water cooled condensers. A final exchange of heat takes place in the residue preheater where the crude oil, overflowing from the last of the series of distillate preheaters, circulates over the coils through which the residue from the hottest still flows. In this way the crude oil has reached the highest

<sup>6 -</sup> Butler, G. M. + Tenney, J. B. - University of Arizona Bulletin - P. 6

-: 

Figure 3.

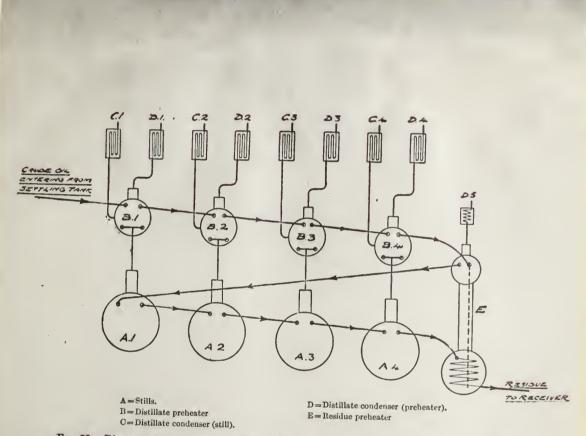
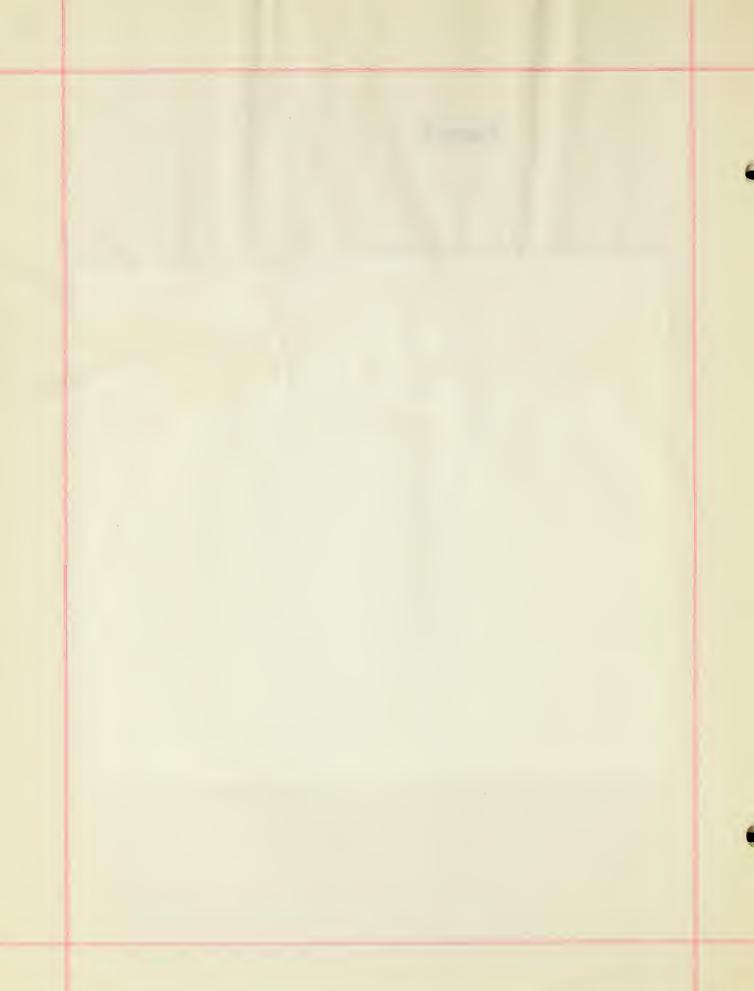


Fig. 56.—Diagram of continuous distillation plant provided with distillate and residue preheater.



temperature possible under the conditions existing, and denuded of its lightest fractions, passes into the first fire heated still. At this point it is much higher in temperature than is possible in a non-preheater system, preliminary heating entailing additional fuel expenditure." Distillates leaving the continuous still condensers pass into various receiving tanks. The residue, now containing only the heavier fractions, passes to the heavy oil stills which are worked under a partial vacuum. The heavy oils and paraffin are distilled over leaving a residue of pitch or coke. (paraffin base oils give a residue of coke while asphalt base oils give a residue of pitch). The heavy oil and paraffin distillate is cooled by refrigeration causing the paraffin to solidify and separate from the heavy oils. The paraffin has many uses one of which is the manufacture of candles. From the filtrate we get our lubricating oils. In the distillation of high boiling point fractions, best results are obtained when the operation is conducted in a current of superheated steam. This prevents "cracking".

Figure 3, page 12, is a diagram of an experimental five.

gallon still. When petroleum is heated in this still the

hydrocarbon with the lowest boiling point distils off first.

By raising the temperature of the oil from time to time, one

after another of the compounds can be distilled off, condensed,

and collected. Thirty five different compounds of the methane

series have been separated from petroleum and their formulas

range from CH<sub>4</sub> to C<sub>35</sub>H<sub>72</sub>.

<sup>6-</sup> Butler, G. M. + Tenney, J. B. - Univ. of Arizona Bulletin -P. 6 9- Campbell, A. - Petroleum Refining - P.P. 121 + 122.

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Figure 4.

A. CAMPBELL.—Petroleum Refining.]

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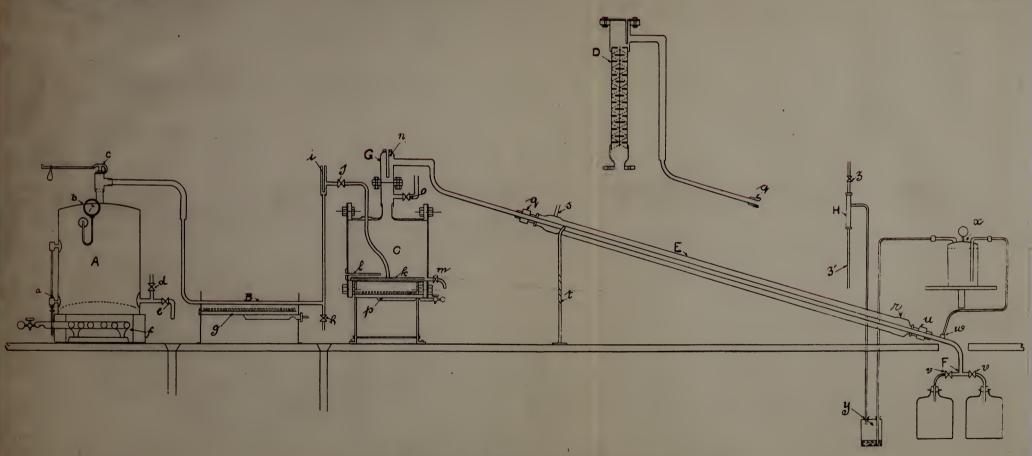
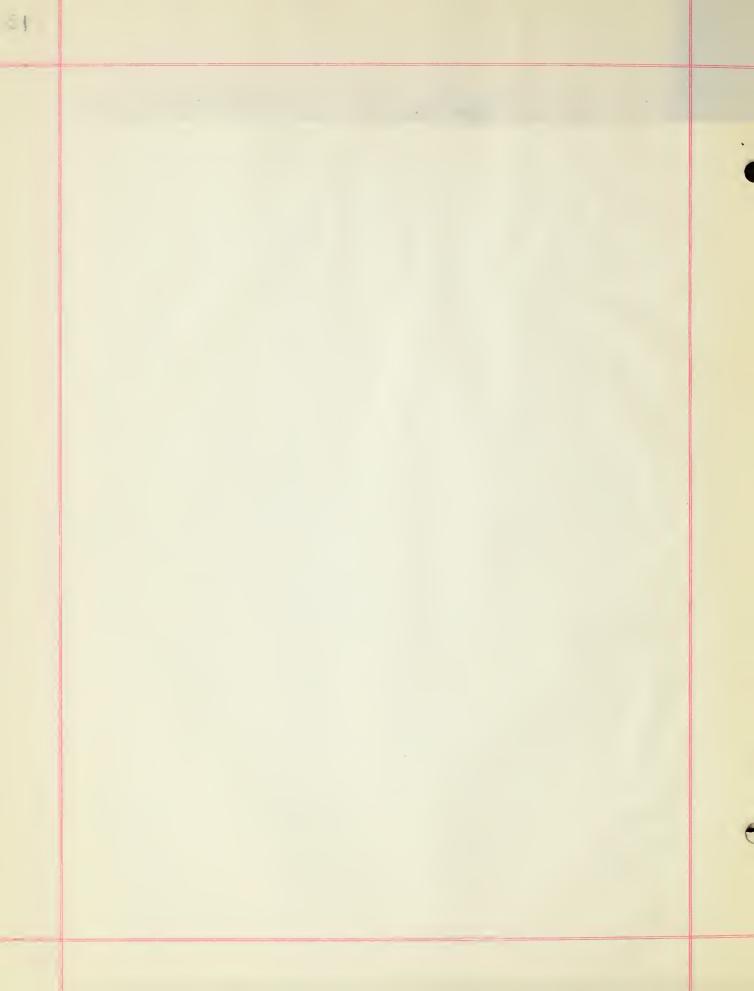


FIG. 20.—EXPERIMENTAL 5-GALLON STILL.



# Explanatory Key to Figure 4.

		,		
	A	Boiler, capacity 10 gallons.	D	Dephlegmator, to replace still-head when desired.
	<i>a</i>	Gauge glass with drain cock to gutter.	q, q	Unions connecting still- head and dephlegmator
	b	Steam gauge, to 40	E	to condenser.
		lbs. per sq. in.	r	Water inlet to condenser.
	c	Safety valve to blow off at 15 lbs. per sq. in.	8	Water outlet from con-
	d	Filling cock from water		denser.
		main.	t	Condenser support.
	e	Blow-off cock delivering into drain connecting	u	Union connecting con- denser to worm-end.
		with gutter.	F	Worm-end.
	f	Three - ring Fletcher	v, v	Worm-end cocks with
	·	burner.	, ,	taper connectors; re-
	В	Steam superheater.		ceivers attached by rubber corks.
	g	Fletcher burner.	G	Still-head.
	h	Drain cock for surplus steam and condensed	n	Thermo-tube for register-
		water; delivering into	"	ing temperature of oil
		drain connecting with		vapours.
		Thormo tubo for register	0	Filling cock.
	i	Thermo-tube, for register- ing temperatures of	p	Three Fletcher's burners in parallel.
		steam.	Н	Vacuum water pump.
	C	Still, capacity 5 gallons.	w	Connection to vacuum
	j	Conc-valve for regulating steam supply to still.		pump.
	k	Steam distributor, per-	x	Vacuum trap and mano- meter.
	n	forated with $32 \times \frac{1}{16}$	y	Mercury back pressure
		inch holes, staggered at 45° from vertical.		safety trap.
	1	Thermo-tube for register-	z	Water-supply cock to
	ι	ing temperature of oil	z'	pump. Compo-tubing allowing
		in still.	~	fall of 20 feet to water
	m	Drain cock.	0	coming from pump.
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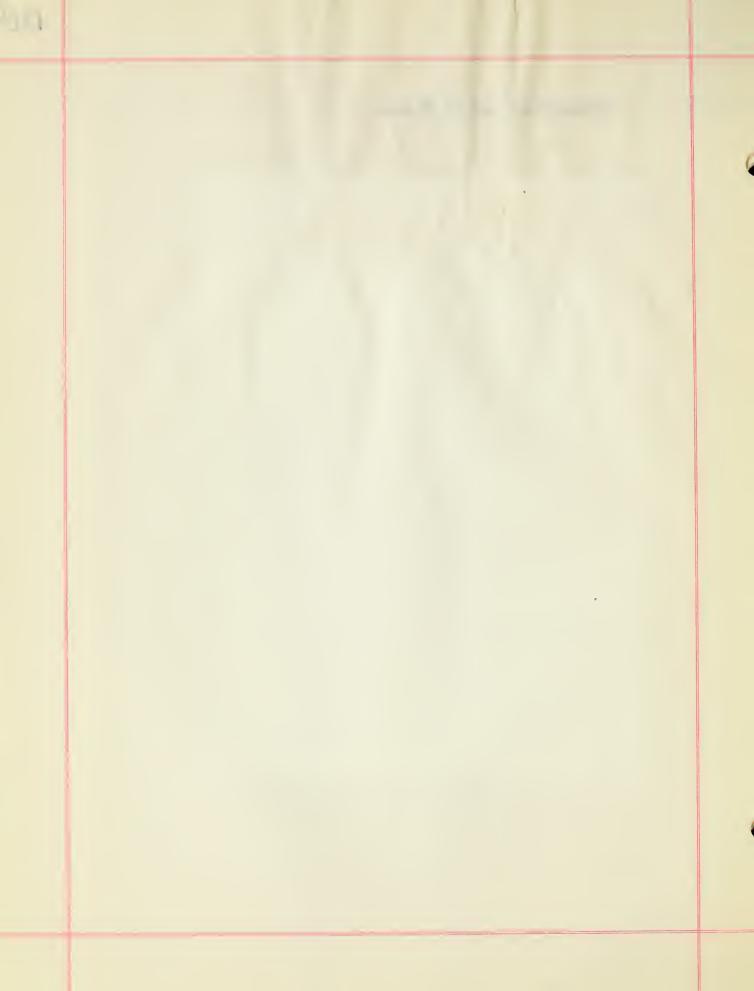
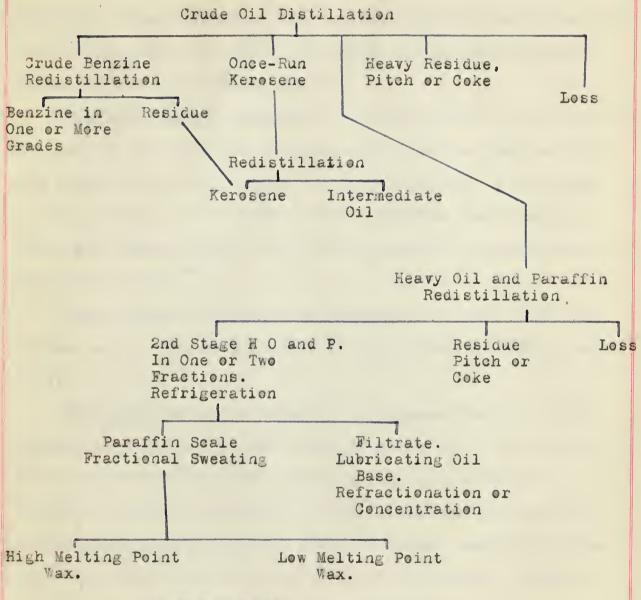
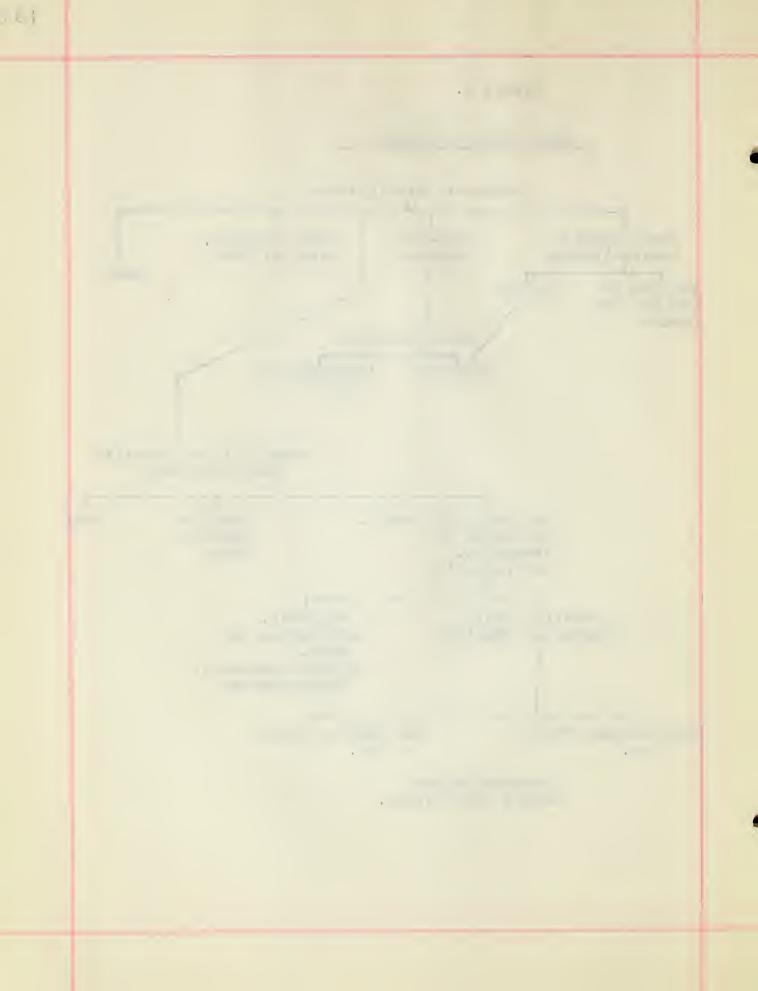


Figure 5.

### FULL REFINING SCHEME



Decolorization Candle Manufacture.



Topping plants: - In many cases especially when asphalt base petroleum is being distilled, no effort is made to obtain the lubricating oil fractions after distilling over the gasoline and part of the kerosene. The residue is drawn out of the still and sold as fuel oil. This procedure is followed in plants which are known as topping plants.

Petroleum ether, ligroin: Petroleum ether is the distillate from petroleum which has a boiling point between 40° and 70° C, and a specific gravity between 0.635 and 0.660. It contains a large amount of the lower paraffin hydrocarbons (heptane C<sub>7</sub>H<sub>13</sub> and hexane C<sub>6</sub>HL<sub>4</sub>), is very inflammable and constitutes a volatile solvent.

Cup grease: - Cup grease is a mixture of heavy oils and calcium soap. The calcium soap is made from tallow and cheap fats.

Petroleum jelly, petrolatum, vaseline: This is a high boiling distillation product made from the still residue left after the distillation of petroleum and has a formula of  $C_{22}H_{46}$  to  $C_{23}H_{48}$ . Vaseline is decolorized by filtering in a heated state through fullers earth or animal charcoal. It is used as a lubricant, rust preventative, in making ointments, and also in making leather dressing and polishes.

Gasoline: - This is one of the low boiling products of the distillation of petroleum, and is commonly understood to be a mixture of hydrocarbons all of which should boil below 225°C

<sup>10 -</sup> Kingzett, C. T. - Chem. Enclyclopedia - P. 693

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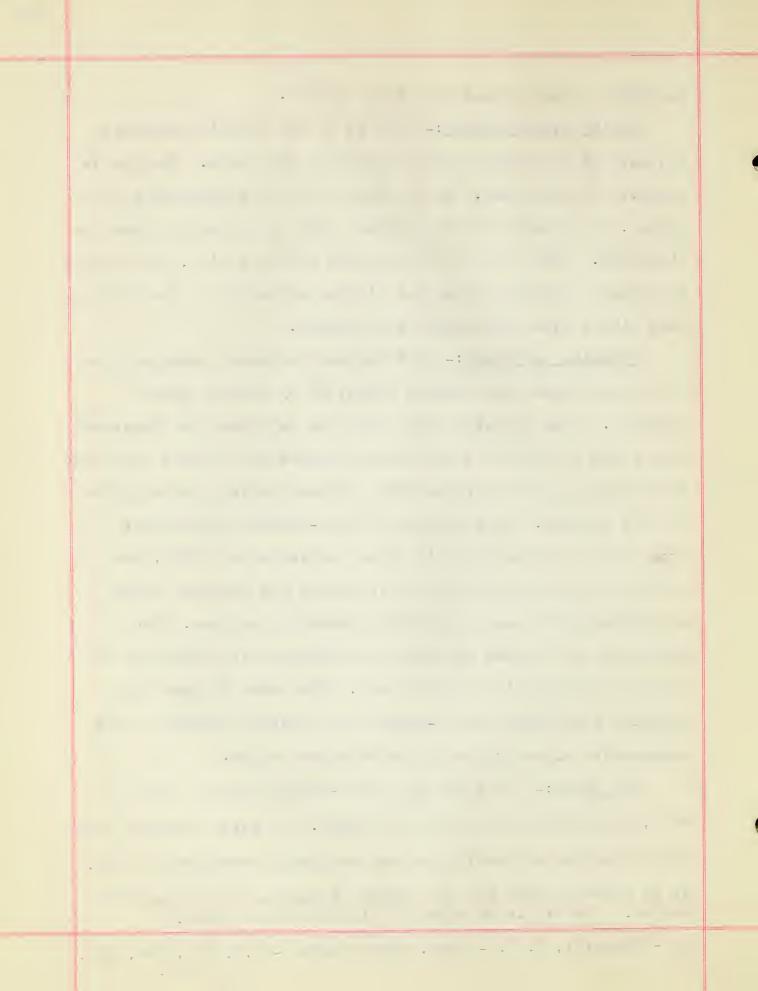
and 90% of which should boil below 190° C.

Casing head gasoline: This is a very volatile gasoline obtained by condensing the gas from the oil wells. The gas is compressed and cooled. By allowing the cold compressed gas to expand, the temperature is lowered until the volatile gases are liquified. This liquid is then mixed with gasoline, the heavier molecules of which prevent the lighter molecules of the casing head liquid from evaporating too rapidly.

Cracking petroleum: - By "cracking" is meant decomposition of the petroleum into lighter fractions by heating under pressure. When the light oils from the petroleum are "cracked" they yield a distillate containing benzene and toluene and large quantities of that material were obtained during the World War by this process. By cracking the high-boiling distillates from crude petroleum that is those boiling above 225°C, low boiling fractions of the paraffin series are obtained which are suitable for use in internal combustion engines. The production of cracked gasoline now exceeds that yielded by the original distillation of petroleum. The gases produced by cracking constitute the by-product and consist chiefly of the unsaturated hydrocarbons of the ethylene series.

Oil Shale: - Oil shale is a fine-grained rock of clay or silt, containing oil yielding material. It has a cleavage like that of slate and constitutes another great storehouse of oil. It is found in many eastern states as well as in the western states. The oil is obtained by distilling the shale.

<sup>10 -</sup> Kingzett, C. T. - Chem. Encyclopedia - P.P. 393, 394, 690, 693 + 801.



## ALIPHATIC HYDROCARBONS

### Saturated Hydrocarbons

The aliphatic hydrocarbons have either a straight chain of carbon atoms or a chain possessing one or more side chains or branches. (see structural formula for normal butane and isobutane Figure A.)

### METHANE SERIES

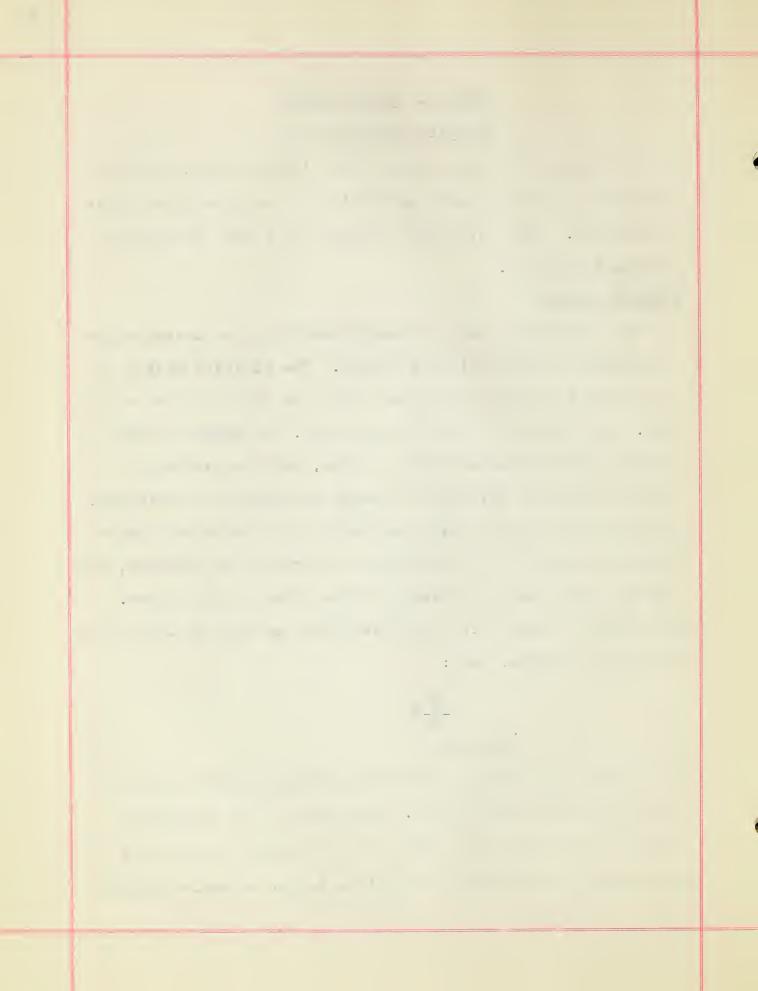
By a straight chain we simply mean that the carbon atoms are joined in one continuous string. The simplest member of this group is naturally the one which contains only one carbon atom. The valence of carbon being four, the number of the hydrogen atoms required would be four, and the resulting compound would be CH<sub>4</sub> which is known as methane or marsh gas. The empirical formula CH<sub>4</sub> gives merely the number and kind of different atoms in the molecule as determined by analysis, but does not show the relationship of the atoms to each other.

An attempt to show this relationship can be made by use of the structural formula, thus:

H\_C-H H\_H

Methane

The lines which join the different symbols represent units of valence and are called bonds. The value of the structural formula lies in the fact that it is an attempt to show the arrangement or grouping of the atoms in the molecule which is



a factor determining the properties of a compound as well as the percentage composition.

The second member of this series is the hydrocarbon containing two atoms of carbon combined with each other and also with as many hydrogen atoms as they are capable of holding. This compound is called ethane and its empirical formula is  $C_2H_6$ . Its structural formula is:

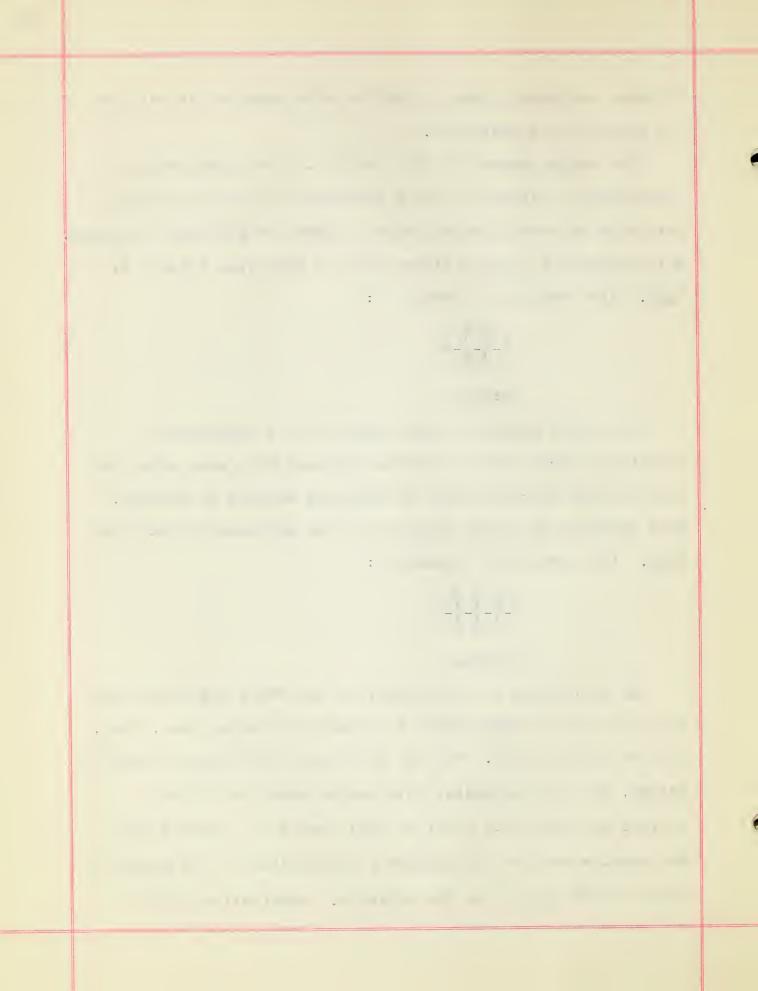
Ethane

The third member of this series is the hydrocarbon containing three atoms of carbon combined with each other and also as many hydrogen atoms as they are capable of holding.

This compound is called propane and its empirical formula is C<sub>3</sub>H<sub>8</sub>. Its structural formula is:

Propane

By proceeding in this manner we can write the structural formulas for the hydrocarbon compounds containing four, five, or more carbon atoms. The one containing four carbon atoms is butane, the one containing five carbon atoms is called pentane and from this point on their names are derived from the Greek words for the numbers corresponding to the number of carbon atoms present in the molecule. Examination of the



empirical formulas of these aliphatic hydrocarbons will prove interesting.

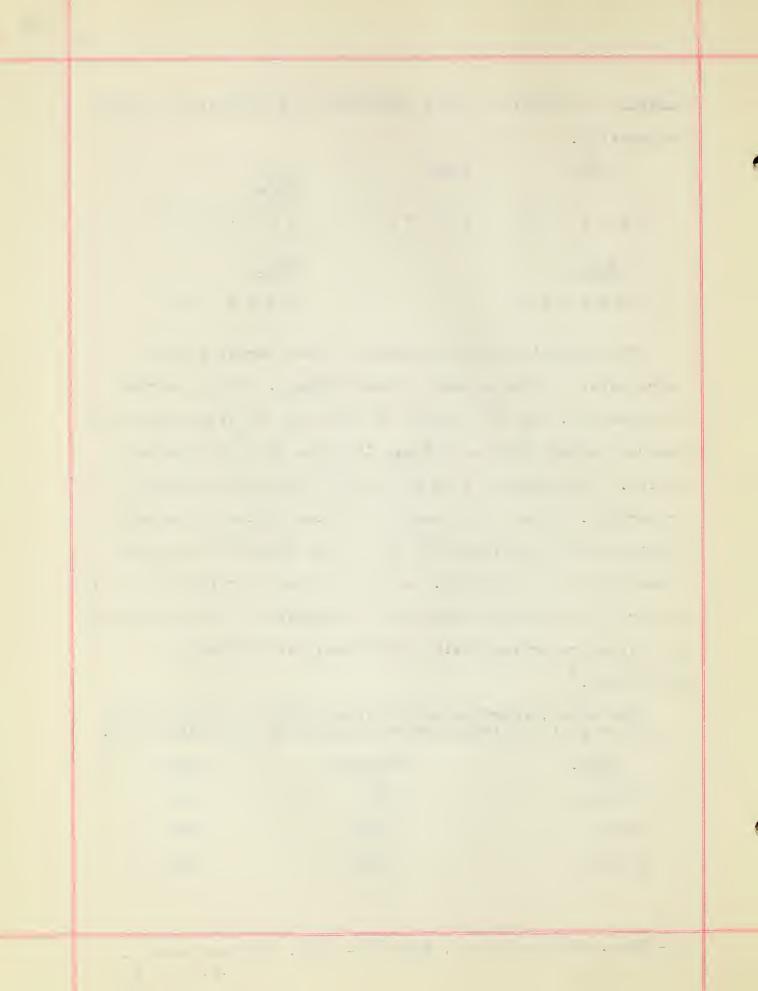
$$C_{1}H_{4}$$
  $C_{2}H_{6}$   $C_{3}H_{8}$ 
 $2 \times 1 + 2 = 4$   $2 \times 2 + 2 = 6$   $2 \times 3 + 2 = 8$ 
 $C_{4}H_{10}$   $C_{5}H_{12}$ 
 $2 \times 4 + 2 = 10$   $2 \times 5 + 2 = 12$ 

The composition of any member of the series can be represented by the general formula  $C_nH_{2n+2}$ . Such a series of compounds, all the members of which can be designated by a general formula such as  $C_nH_{2n+2}$  is known as an homologous series. The members of an homologous series have similar properties. There are a number of these series in organic chemistry and the members of each group bearing a striking resemblance to each other. A study of the characteristics of one or two members of each group or series and the underlying principles regarding their relationship is frequently sufficient.

The names, formulas and physical states of some of the members of the methane series is given in the table below.

Name.	Formula	State
Methane	CH <sub>4</sub>	Gas
Ethane	C <sub>2</sub> H <sub>6</sub>	Gas
Propane	C <sub>3</sub> H <sub>e</sub>	Gas

s - Chem. Warfare School, Book II - Chem. Warfare Agents - P.P. 72 + 73



Name	Formula.	State
Butane	CaHlo	Gas
Pentane	C <sub>5</sub> H <sub>12</sub>	Liquid
Hexane	C <sub>6</sub> H <sub>14</sub>	Liquid

11

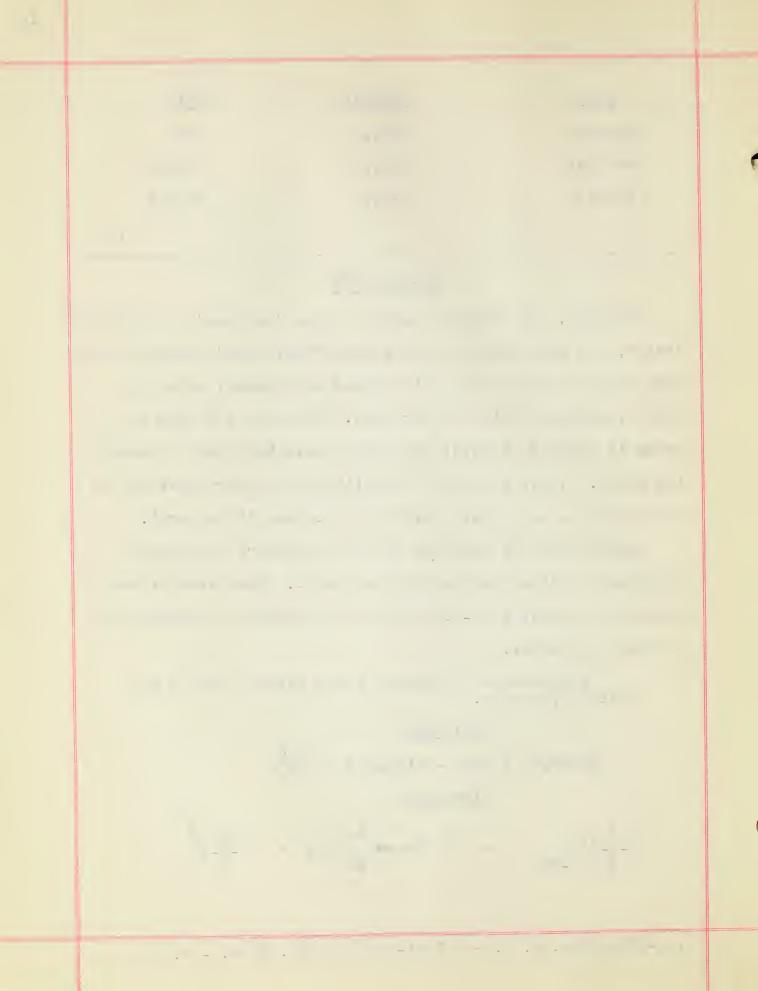
# Methane CH4

Methane, the simplest member of the "methane" or "paraffin" series, has been given a common name "marsh gas" and gets this name from the fact that it is formed in stagnant water in which vegetable matter is decaying. When the soft mud of a swamp is stepped on marsh gas may be seen bubbling up through the water. It is the chief constituent of natural gas and is also found in coal mines where it is called "fire damp".

Methane may be prepared in the laboratory by heating anyhydrous sodium acetate with an alkali. Best results are obtained by using soda-lime which is a mixture of sodium and calcium hydroxides.

Preparation of Methane using sodium acetate and sodium hydroxide.

# Structural



Preparation of methane using sodium acetate and soda-lime.

### Empirical

$$3 \text{ NaC}_2\text{H}_3\text{O}_2 + \text{NaOH} + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + 2\text{Na}_2\text{CO}_3 + 3 \text{ CH}_4$$

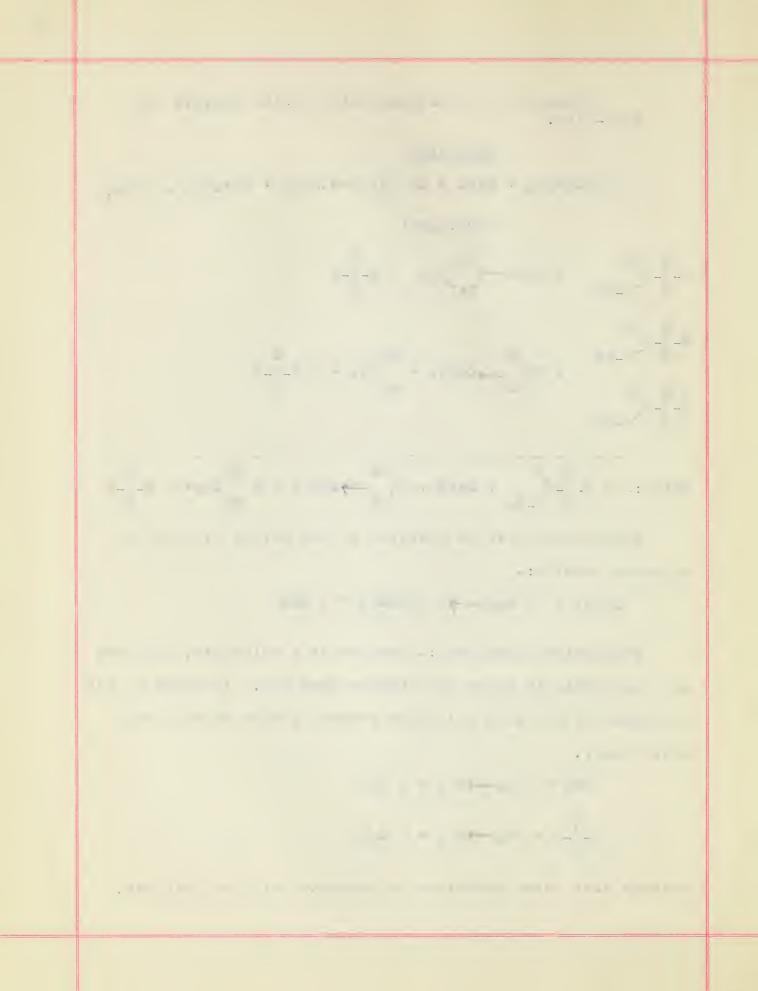
#### Structural

Methane may also be prepared by the action of water on aluminum carbide:-

Properties of Methane: - Methane is a colorless, odorless gas, insoluble in water and lighter than air. It burns in air or oxygen with a pale hot flame forming carbon dioxide and water vapor.

$$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O$$

Methane also forms substitution products with the halogens.



Substitution products of methane: - A reaction in which an element is removed from a compound and another element is put in its place is known as a reaction of "substitution", and the compound formed is called a "substitution product".

With proper conditions the hydrocarbon compounds of the methane series may react with the halogens in such a way that the atoms of the halogens will replace the hydrogen atoms of the hydrocarbons forming substitution products of the hydrocarbons. The chlorine substitution products of methane are given in the table below:-

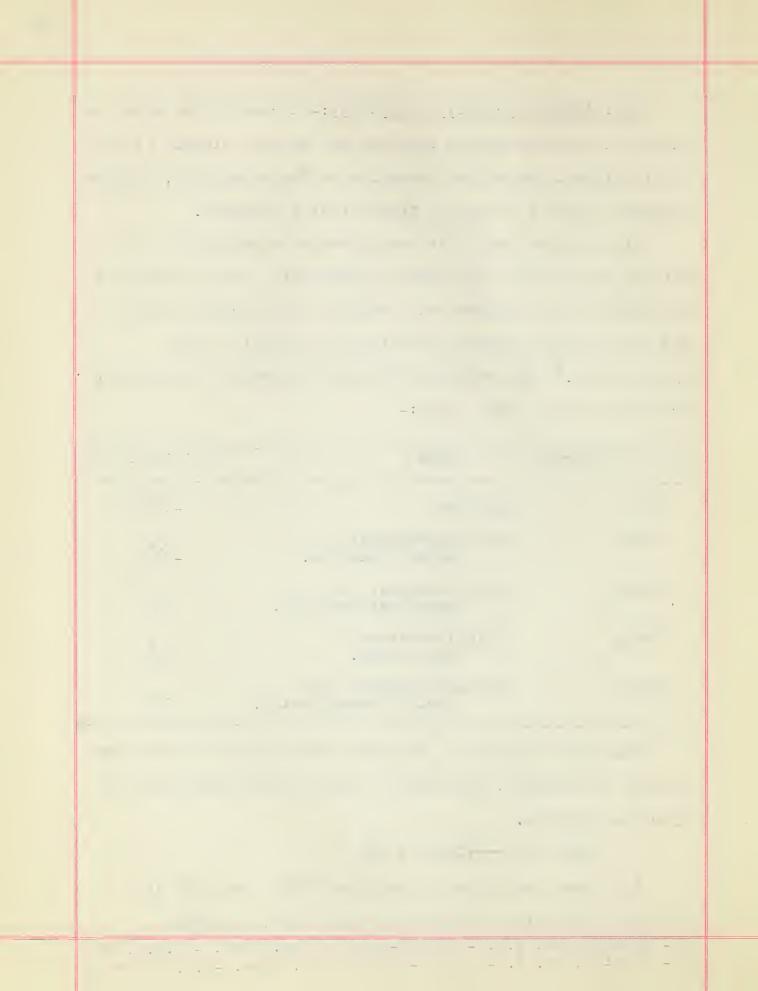
Molecular Formula	Name	Boiling Point
CH <sub>4</sub>	Methane	-164°
CH <sub>3</sub> Cl	Monochlormethane or Methyl Chloride.	-24°
CH <sub>2</sub> Cl <sub>2</sub>	Dichlormethane or Methylene Chloride.	41°
CHCl3	Trichlormethane or Chloroform.	61°
CCl4	Tetrachlormethane or Carbon Tetrachloride.	76°

When equal volumes of chlorine and methane are mixed and exposed to sunlight, they react forming monochlormethane and hydrogen chloride.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

If a tube containing the mixture (CH<sub>3</sub>Cl and HCl) is inverted over brine and left for some hours, a gradual

<sup>4 -</sup> Chamberlain, J.S. - A Text-book of Org. Chem. - P.P.6,7+9
12- Schmidt, Dr. J. - A Text-book of Org. Chem. -P.P. 122 + 123



contraction occurs to about one half the original volume. The remaining gas has a molecular formula of CH3Cl. The other product of the reaction is HCl which is readily soluble in brine. Since monochlormethane (methyl chloride) is insoluble in brine it remains as a gas in the tube. This reaction is a direct substitution reaction. By increasing the quantity of chlorine and repeating the process, the remaining hydrogen atoms may be substituted, yielding products having the following formulas:-

CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>.

Chloroform: - Chloroform is a substitution product of methane and may be prepared by the distillation of aqueous alcohol with bleaching powder. Chloroform is a heavy colorless liquid having a characteristic ethereal odor and a sweet taste. It is only slightly soluble in water and when pure is a valuable anaesthetic.

<u>Carbon Tetrachloride</u>: - Carbon Tetrachloride is made by passing chlorine into carbon bisulphide. The chlorination of the carbon bisulphide is effected with the aid of aluminum chloride or manganese chloride as a catalytic agent.

CS<sub>2</sub> + 3 Cl<sub>2</sub> - CCl<sub>4</sub> + S<sub>2</sub>Cl<sub>2</sub>
Sulphur Chloride

The carbon tetrachloride and sulphur chloride may be separated by fractional distillation.

Properties of carbon tetrachloride: - Carbon tetrachloride

<sup>12 -</sup> Schmidt, Dr. J. - A Text-book of Org. Chem. -P.P. 122+123
13 - Read, John - A Text-book of Org. Chem. - P. 114

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is a heavy colorless liquid with an odor somewhat resembling chloroform. It is non-flammable and a good solvent which makes it valuable in removing grease spots from clothing. Its non-flammable property makes it valuable for use in fire extinguishers. The liquid quickly vaporizes when put on a fire forming a heavy gas which extinguishes the fire by settling over the burning material and shutting out the air.

Synthesis of ethane: - Because of the chemical inertness of the paraffine, it is not possible to build up the molecule of a higher homologue from two or more molecules of lower homologues by any direct process such as represented by the following equation: -

# It is not possible to do this

Even though the two hydrogen atoms may not be eliminated directly leaving the CH<sub>3</sub> groups to tie up as indicated, the synthesis can be accomplished in an indirect manner. In order to do this the methane must first be converted into methyl chloride (monochlormethane). Methyl chloride is much more active than methane and by means of metallic sodium, it is possible to remove the chloring atoms from two molecules leaving the two CH<sub>3</sub> groups to unite with each other, thus,

$$CH_3C1 + 2 Na + C1CH_3 \rightarrow 2 NaC1 + C_2H_6$$

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#### Structural formula

By this process the synthesis of ethane has been effected in two stages, first the preparation of methyl chloride, and second the reaction of sodium and methyl chloride. Methyl iodide however reacts more readily with sodium and for this reason is generally used in the actual preparation of ethane. By extending this method the synthesis of other members of the series may be accomplished.

ethyl chloride methyl chloride propane

ethyl chloride ethyl chloride

butane

13

The methyl chloride for the preceding reactions can be prepared by the action of hydrochloric acid on wood alcohol. (see page

The ethyl chloride for the preceding reactions can be prepared by the action of hydrochloric acid on grain alcohol. (see page 66)

Names of Some of The Paraffin Radicals:-

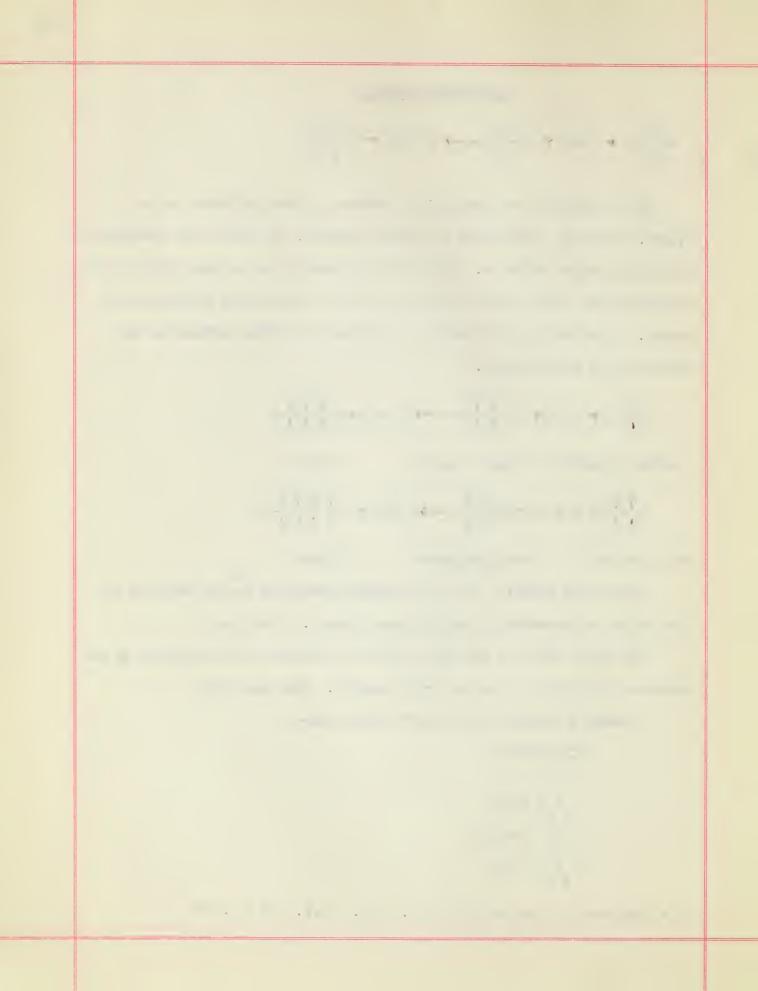
C H - ethyl

2 5

C H - propyl

C H - butyl

13 - John Read - A Text-book of Org. Chem. - P.P. 119 & p. 120



Properties of ethane; - Ethane is a colorless, tasteless gas with an agreeable ethereal odor. It resembles methane very closely in its chemical and physical properties. It is made on a large scale by the combination of ethylene (C H ) with hydrogen in the presence of finely  $\begin{array}{c} 2 & 4 \\ 2 & 4 \\ 2 & 4 \\ 3 & 4 \\ 4 &$ 

## Unsaturated Hydrocarpons

#### ETHYLENE SERIES OR OLEFINES.

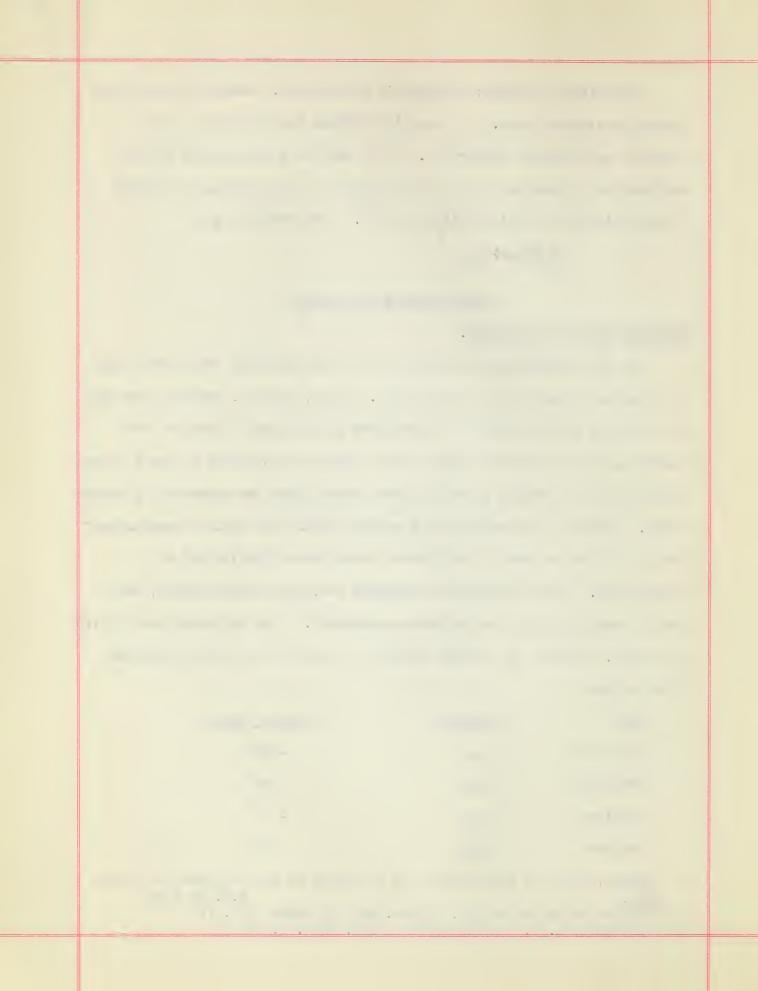
In the hydrocarbons considered up to this point no two carbon atoms were united by more than a single bond. It is, however, possible for any two adjacent carbon atoms in the molecule to be united by two or even three bonds, but compounds whose carbon atoms are connected by two or three bonds are not as stable as those whose carbon atoms are connected by single bonds. Compounds possessing these multiple bonds are called "unsaturated" because all the valence of the carbon atoms is not "satisfied" or "saturated". These unsaturated compounds are, as we would expect, more active chemically than the saturated compounds. The following table gives the names, formulas and boiling points of a few of the first members of this series;-

Name	Formula	Boiling Point
Ethylene	C <sub>2</sub> H <sub>4</sub>	-103°
Propylene	C <sub>3</sub> H <sub>6</sub>	- 48°
Butylene	C <sub>4</sub> H <sub>8</sub>	<b>-</b> 5°
Amylene	C <sub>5</sub> H <sub>10</sub>	39° 11

<sup>5 -</sup> Remsen, Ira - An Introduction to the Study of the Compounds of Carbon Chem. P.P. 24 & 277

11 - Holleman, A. F. - A Text-book of Org. Chem. P. 132

<sup>3 -/</sup>Warfare School - Book II, - Chem. Warfare Agents - P. 73



By observing the formulas in the above table it will be noticed that there are always twice as many hydrogen atoms in the molecule as there are carbon atoms. Therefore we write the general formula for this series as follows:-

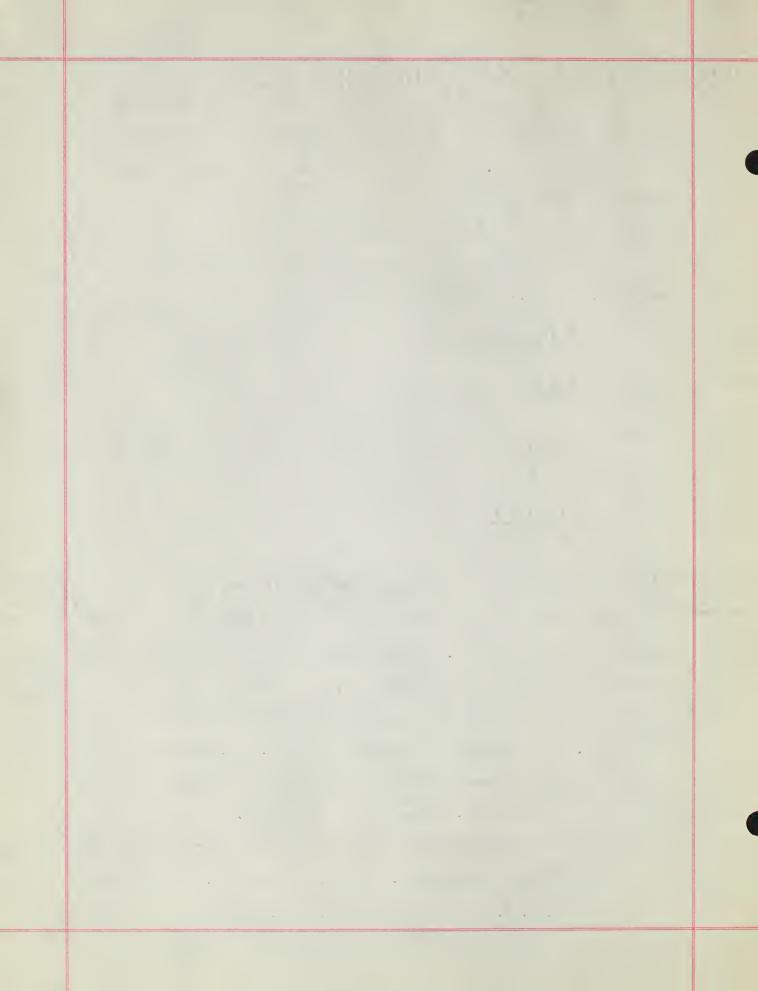
It is customary to write the structural formulas for ethylene, propylene, butylene, and amylene as follows;-

# Ethylene

Ethylene is the first member of this series generally known as the ethylene series or olefines. It is prepared by heating ethyl alcohol with an excess of sulphuric acid (see page 65).

Ethylene is a colorless gas with a sweetish odor, and burns with a smoky flame. It forms explosive mixtures with air. Dr. Luckhardt, of the University of Chicago, has shown that ethylene is a powerful anesthetic and has some advantages over nitrous oxide. It is produced in the destructive distillation of coal and has been introduced in California for coloring mature citrous fruits. (lemons, oranges, etc.)

4 - Chamberlain, J. S. - A Text-book of Org. Chem. P. 160



Ethylene reacts energetically with chlorine and with bromine.

$$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$$

ethylene bromide

The reaction is probably due to the fact that ethylene is an unsaturated hydrocarbon. The following equation which contains structural formulas shows how the reaction of ethylene with bromine is probably one of "saturation".

In the presence of platinum black, ethylene will combine with hydrogen at ordinary temperatures yielding ethane.

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$
 14

As a general rule the halogen substitution products of the unsaturated hydrocarbons cannot be prepared by direct action of the halogens since addition products result. They can be produced, however, by the action of alcoholic potassium hydroxide on the disubstituted hydrocarbons. This action occurs very readily if the addition products of the ethylene series are used.

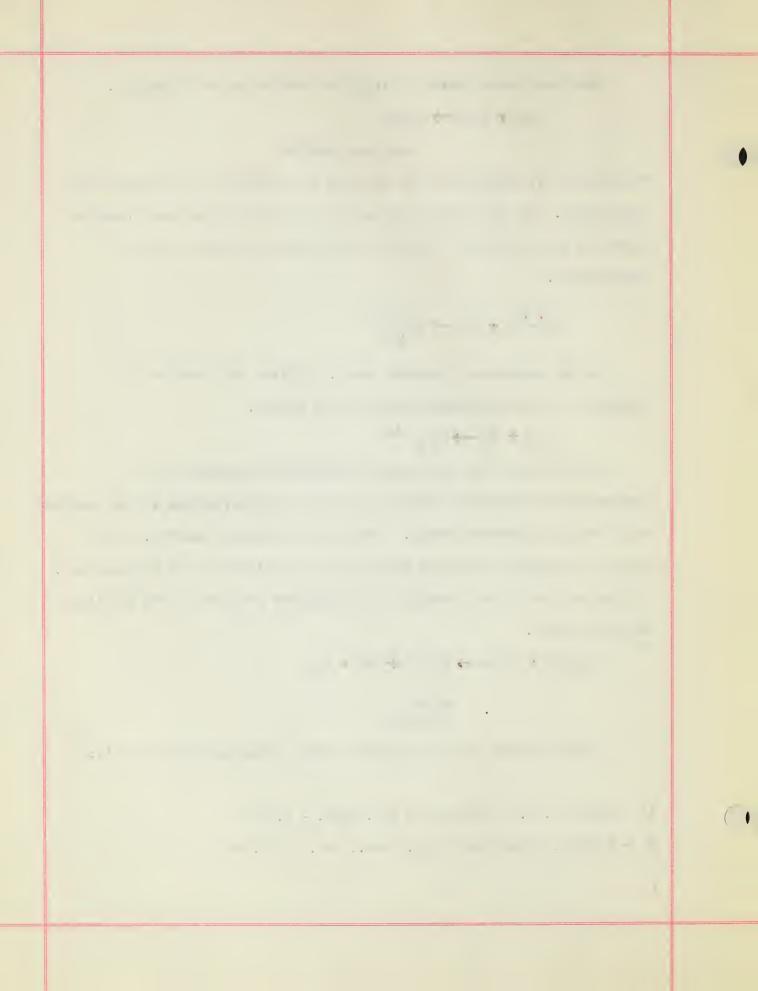
$$c_2H_4cl_2 + koh \longrightarrow c_2H_3cl + kcl + H_2o$$

vinyl chloride

The equation for this reaction (using structural formulas) is:-

14 - Cohen, J. B. - Theoretical Org. Chem. - P. 247

15 - Richter, Victor Von - Org. Chem., Vol. I - P. 96



In a similar manner:-

$$c_3H_6c1_2 + KOH \longrightarrow c_3H_5c1 + KC1 + H_2O$$

Propene Allyl chloride chloride

$$C_4H_8C1_2 + KOH \longrightarrow C_4H_7C1 + KC1 + H_2O$$

Butene Crotomyl chloride chloride

$$C_5H_{10}C1_2 + KOH \longrightarrow C_5H_9C1 + KC1 + H_2O$$

Pentene Chlorochloride pentene

Although ethylene is not acted on directly by HCl, it combines directly with concentrated hydrobromic and hydriodic acids at 100°, forming respectively ethyl bromide and ethyl iodide.

$$C_2H_4 + HBr \longrightarrow C_2H_5Br$$

$$C_2H_4+HBr \longrightarrow C_2H_5Br$$

Another method for the preparation of ethylene is to treat ethyl bromide with an alcoholic solution of potassium hydroxide.

$$C_2H_5Br + KOH \longrightarrow C_2H_4 + H_2O + KBr$$

. . ( 3 + + -. United the second sec 4In a similar manner:-

$$c_{3}H_{7}c_{1} + KOH \longrightarrow c_{3}H_{6} + KC_{1} + H_{2}O$$

$$c_{4}H_{9}c_{1} + KOH \longrightarrow c_{4}H_{8} + KC_{1} + H_{2}O$$

$$c_{5}H_{1}C_{1} + KOH \longrightarrow c_{5}H_{1}O + KC_{1} + H_{2}O$$
16

## Unsaturated Hydrocarbons

#### ACETYLENE SERIES

We have previously stated that unsaturated compounds may have three bonds between carbon atoms. Acetylene is an example of an unsaturated compound in which there are three bonds between carbon atoms (H-CEC-H). This compound is the first member of a series that bears its name and the members of this series are called acetylenes. The following table gives the names, formulas, and boiling points of some of the first members of this series:-

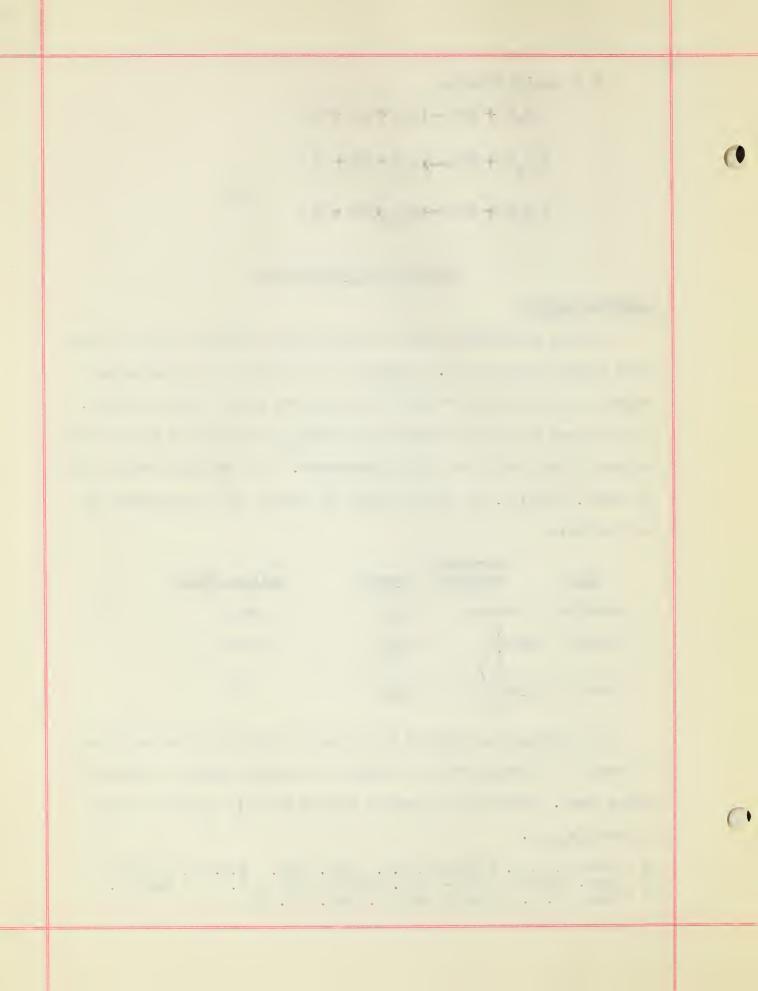
Name	Structural Formula	rormula	Boiling Point
Acetylene		C2H2	Gea
Propine	H-C=C-C-H H H	C3H4	Gas
Butine	н • н-с=с-ç-ç-н н н	C4H6	18

By observing the formulas in the above table it will be seen that the number of hydrogen atoms is always two less than twice the number of carbon atoms. Therefore the general formula for this series is always written  $C_nH_{2n-2}$ .

14

16 - Perkins, W. H. & Kipping, F.S. - Org. Chem. - P.P. 76, 81 & 82 3 - Chem. Warfare School - Chem. Warfare Agents - P. 74 - Book II.

14 - Cohen, J. B. - Theoretical Org. Chem. - P. 257



Acetylene is a colorless gas that burns with a brilliant flame giving a very satisfactory light and is prepared by the action of water on calcium carbide(CaC2).

$$CaC_2 + H_2O \longrightarrow C_2H_2 + CaO$$

"An important property of acetylene is the ease with which it forms

4

metallic compounds especially with silver and copper".

When acetylene is passed into an ammoniacal solution of cuprous chloride (CuCl), a reddish brown precipitate of copper acetylide( $C_2Cu_2$ ) is formed.

2 
$$\operatorname{CuCl} + \operatorname{C}_2\operatorname{H}_2 \longrightarrow \operatorname{C}_2\operatorname{Cu}_2 + 2 \operatorname{HCl}$$

This reaction serves as a delicate test for acetylene and the separation of acetylene from other gases can be effected by passing the gases through the armoniacal solution of cuprous chloride. Dry copper acetylide explodes when struck or submitted to a shock or when heated to about 120°C. It is decomposed by hydrochloric acid forming acetylene.

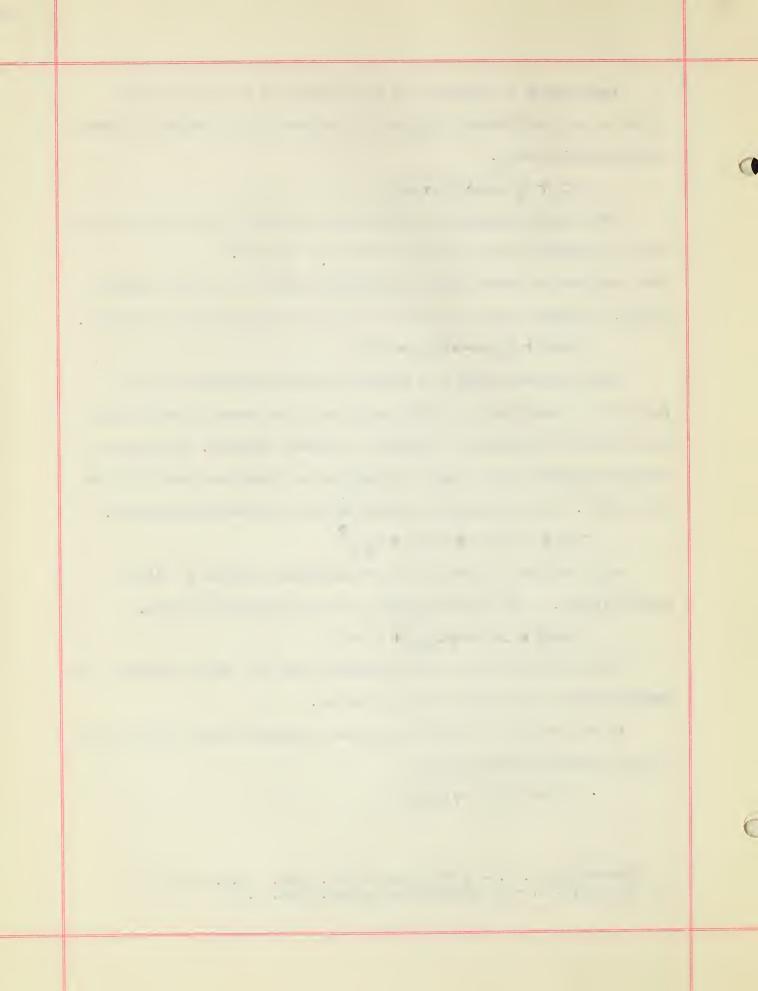
When acetylene is passed into an ammoniacal solution of silver chloride(AgCl), a white precipitate of silver acetylide is formed.

$$2 \text{ AgCl} + \text{ C}_2\text{H}_2 \longrightarrow \text{ C}_2\text{Ag}_2 + 2 \text{ HCl}$$

Silver acetylide is far more explosive than the copper compound, and 7 detonates when it is gently rubbed or heated.

In the presence of antimony chloride, acetylene unites with chlorine forming tetrachlorethane(C,H,Cl,)

<sup>4 -</sup> Chamberlain, J. S. - A Text-book of Org. Chem. - P.P. 162 & 163 7 - Williams, R. J. - An Introduction to Org. Chem. P. 44



When acetylene comes in contact with liquid bromine cooled in ice, it is absorbed by the bromine with the formation of tetrabromoethane  $(C_2H_2Br_4)$ .

$$C_2H_2 + 2 Br_2 \longrightarrow C_2H_2Br_4$$

Another way that acetylene can be prepared is by treating vinyl bromide ( $C_2H_3Br$ ) with an alcoholic solution of potassium hydroxide.

$$C_2H_3Br + KOH \longrightarrow C_2H_2^{\uparrow} + KBr + H_2O$$

If dibromoethane (C2H4Br2) is treated with an alcoholic solution of potassium hydroxide vinyl bromide is first formed and then the potassium hydroxide reacts with the vinyl bromide forming acetylene. The process occurs in two steps the equations for which are as follows:-

(1) 
$$C_2H_4Br_2+KOH \longrightarrow C_2H_3Br+KBr+H_2O$$

(3) 
$$C_{24}Br_{2} + 2 KOH \longrightarrow C_{2}H_{2} + 2 KBr_{2} + 2 H_{2}O$$

In a similar manner propine and butine can be prepared:-

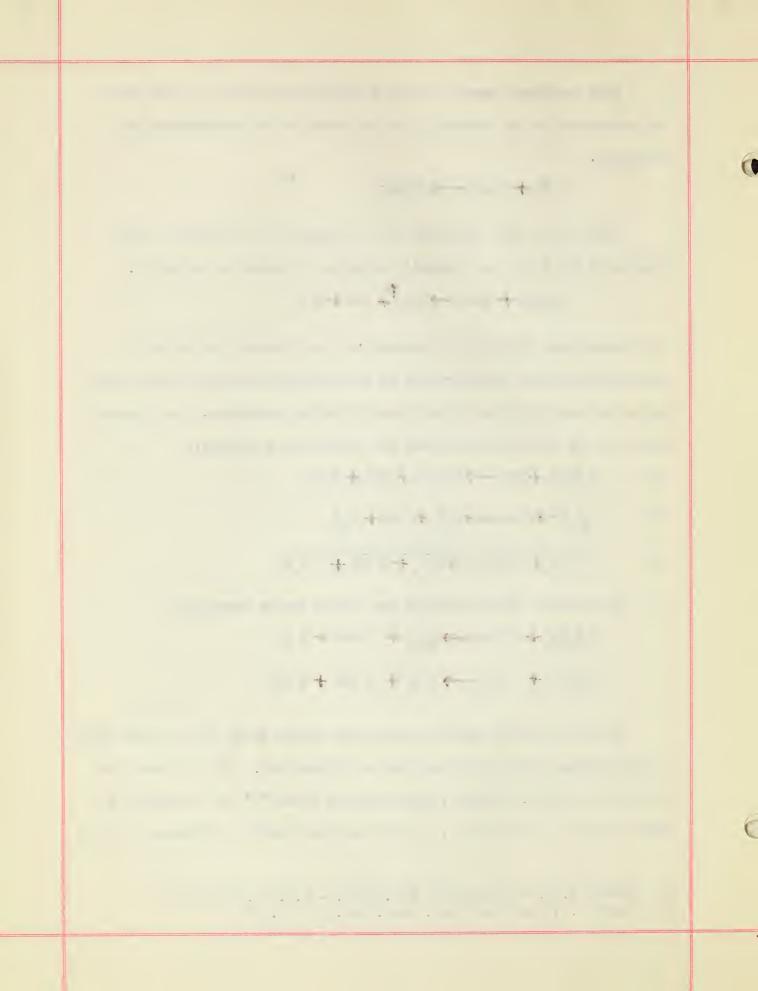
$$c_3H_6Br_2 + 2 KOH \longrightarrow c_3H_4 + 2 KBr + 2 H_0$$

$$C_{48}H_2 + 2 KOH \longrightarrow C_{46}H_6 + 2 KBr + 2 H_2O$$

14 & 15

In the preceding pages we have taken up the study of the three series of hydrocarbons which are classified as "Aliphatic". If we compare the formulas of ethane, ethylene, and acetylene using "n" for the number of carbon atoms in the molecule, we find that the number of hydrogen atoms is

14 - Cohen, J. B. - Theoretical Org. Chem. - P.P. 92, 259 & 263 15 - Richter, Victor Von - Org. Chem. Vol. 1, - P. 96



represented by 2n + 2, 2n, and 2n -2 respectively.

All members of the methane series are represented by the general formula C H n 2n + 2

All members of the ethylene series are represented by the general formula  ${\tt C}_n{\tt H}_{2n}$  .

All members of the acetylene series are represented by the general formula C H  $_{\rm n}$  2n - 2  $^{\circ}$ 

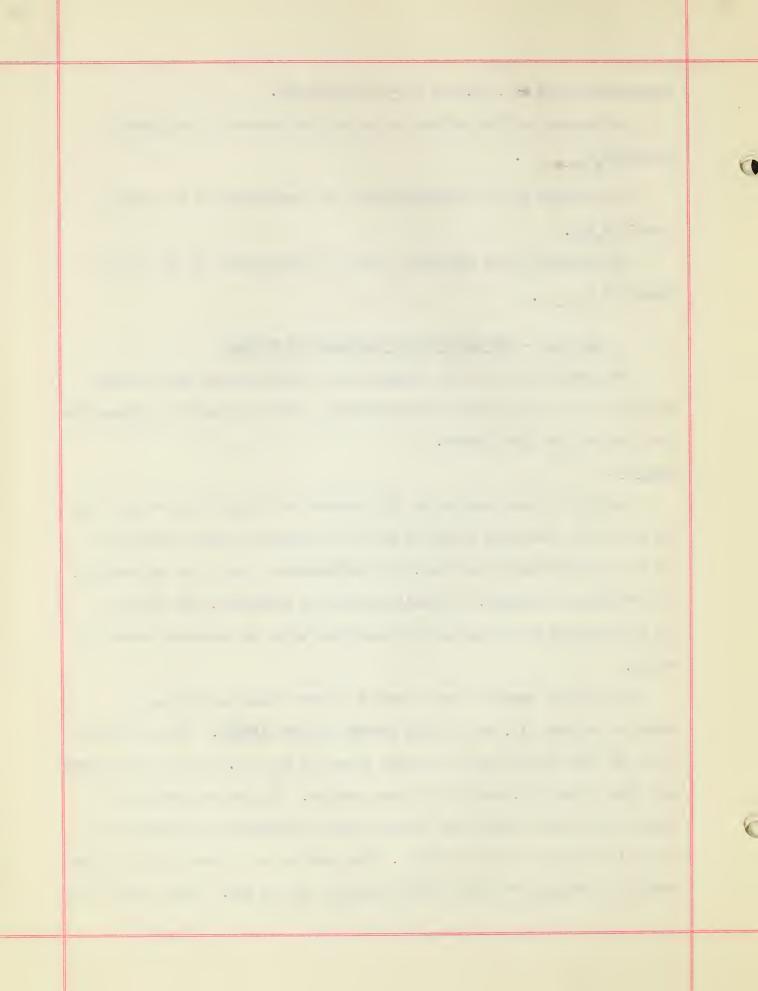
#### COAL GAS - THE DESTRUCTIVE DISTILLATION OF COAL

The consideration of the destructive distillation of coal belongs with the study of the aromatic hydrocarbons, since our aromatic hydrocarbons are obtained from that source.

#### Coal Gas:

Coal gas is manufactured by the destructive distillation of coal and the series of operations connected with its preparation and distribution are (1) distillation of the coal, (2) condensation of coal tar and armonia, (3) scrubbing or washing, (4) purification, (5) measuring, (6) storing, (7) distribution of the gas to the mains from which the customer draws his supply.

The coal is charged into firebrick retorts which are afterwards sealed to exclude air, and is then heated to about 1300°C. The coal first fuses and then "boils" and in boiling gives off the gas. When all the gases have been driven off, nothing but coke remains. The gas on leaving the retort passes into a pipe line leading into the hydraulic main which is a large pipe partly filled with water. The water extracts some of the tar and ammonia in the gas and also prevents backflow of the gas. After leaving the



hydraulic main the gas passes to the condenser where it goes through a series of pipes surrounded by water. The water cools the gas and the tar settles out. An exhauster located between the hydraulic main and the condenser draws the gas from the retorts and forces it on its way toward the storage tanks. From the condenser the gas passes to the scrubber which is a cylindrical tower filled with wooden grids. Water sprayed in at the top of the tower passes over the grids and absorbs any ammonia, or ammonia compounds and removes some of the hydrogen sulphide and other impurities. The ammoniacal liquor drops to the bottom of the scrubber and is drained off. The gas next goes to the purifiers in order to remove the remaining hydrogen sulphide. The purifiers are steel boxes equipped with wooden trays upon which a mixture of wood shavings and iron oxide (rust) is placed. The hydrogen sulphide is removed by combining with the iron oxide. The shavings keep the iron oxide porous so that greater surface is exposed for contact with the gas. The gas which is now pure and ready for use goes through a large meter which records its volume and is then stored in the gas holder from which it flows into large mains for distribution to the customers.

## Water Gas:

Water gas is a mixture of carbon monoxide and hydrogen and is made by passing steam through coke or anthracite coal heated to incandescence. The hot coke reduces the steam forming carbon monoxide and hydrogen.

Carburetted water gas is manufactured by passing steam through coke heated to incandescence and adding gas oil to enrich or carburet the water gas. The plant consists of a generator, a carburettor and a superheater.

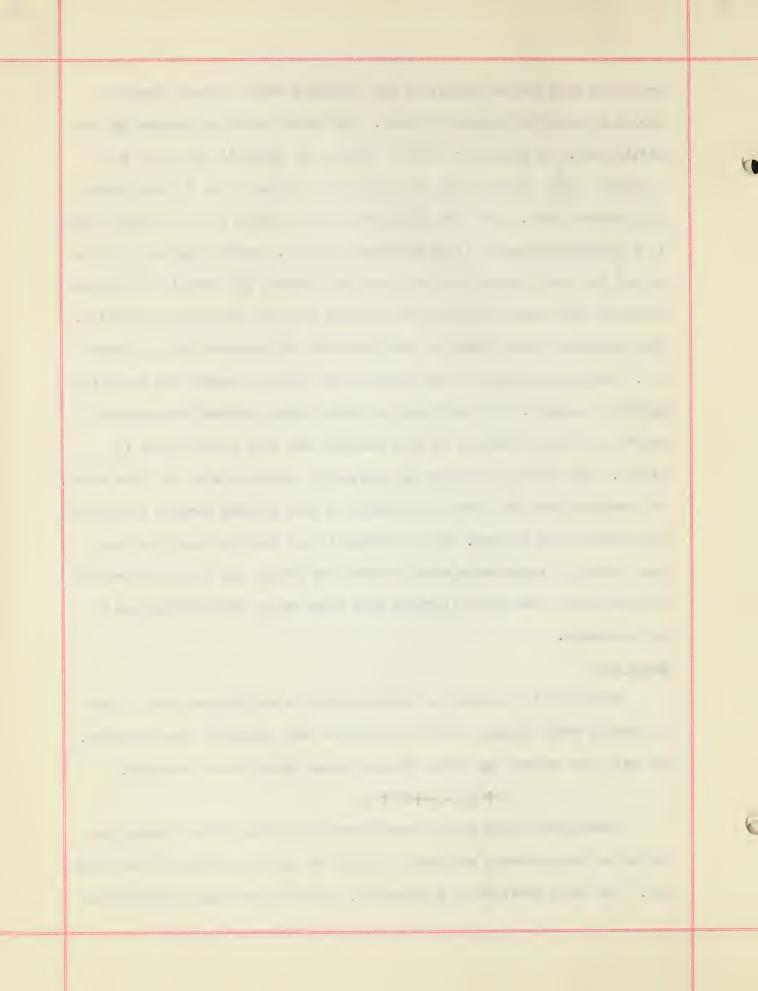
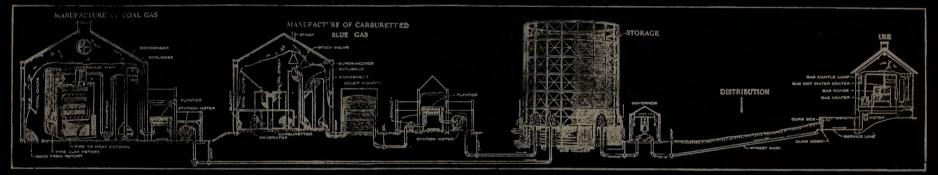


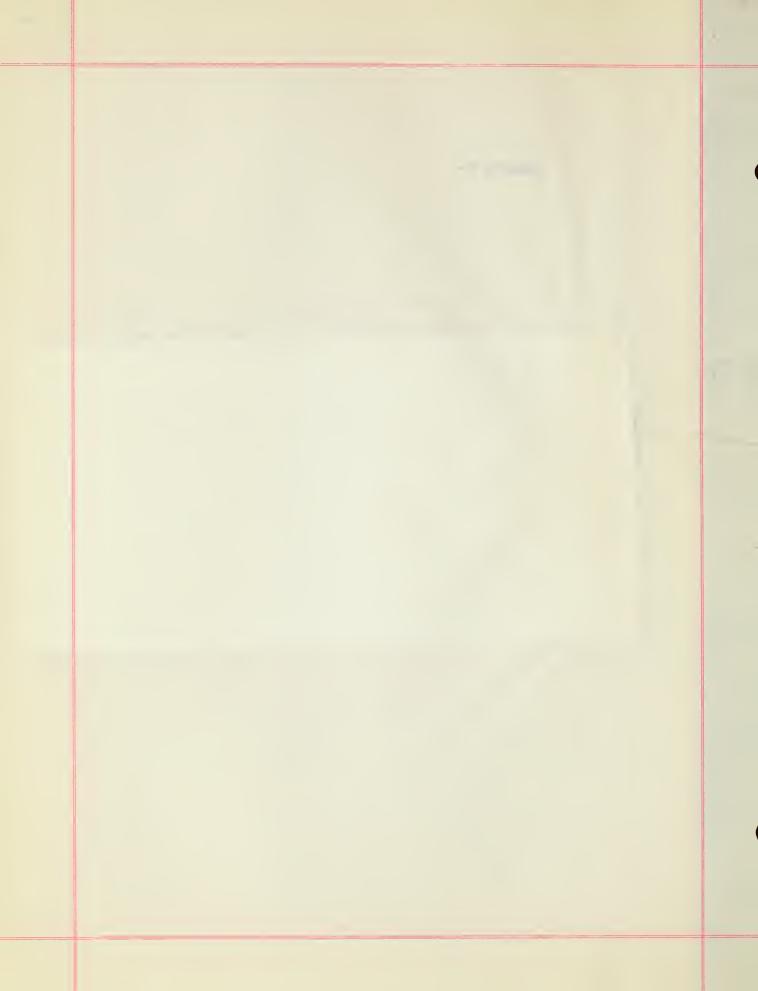
Figure 6.

# How Manufactured Gas Is Made and Distributed



Model Showing How Coal Is Transmuted Into Gas and Delivered to the Home. Original in Smithsonian Institution, U.S. National Museum, Washington, D.C.

7

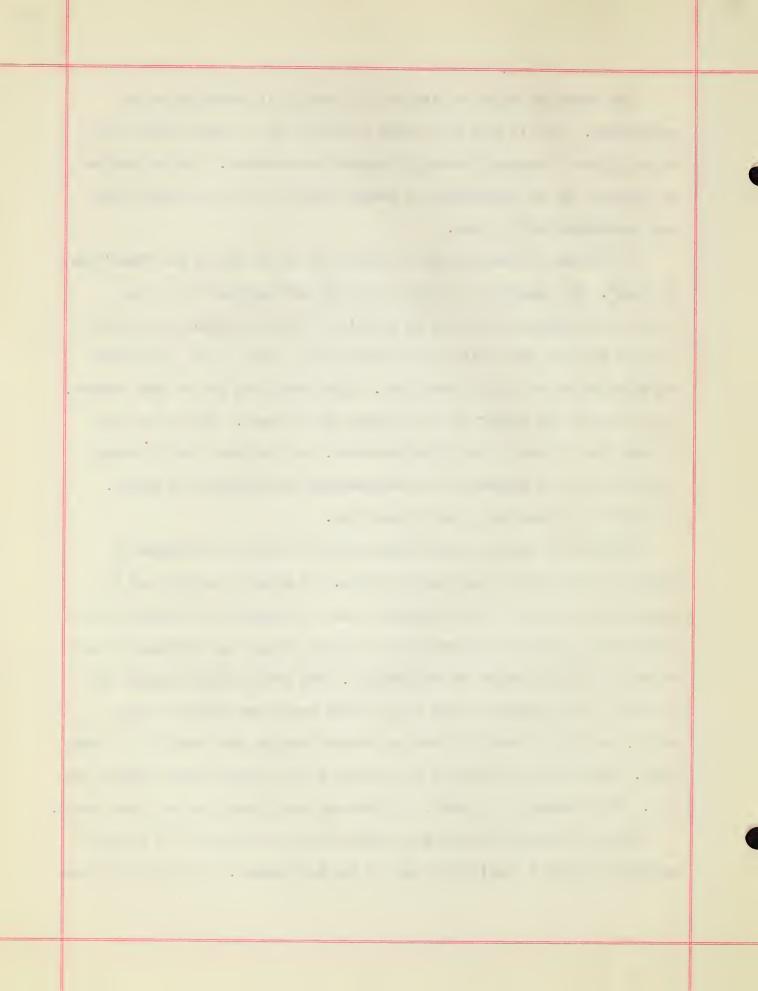


The generator which is lined with firebrick is connected to the carburettor. This is also lined with firebrick and is almost filled with bricks placed cris-cross forming a honeycomb arrangement. The carburettor is connected to the superheater, a vessel similar to the carburettor and also honeycombed with bricks.

The process of manufacture is carried on in two steps, the "blow" and the "run". The generator is filled with coke and anthracite coal and ignited and burned with the aid of a blast of air from a blower until the coke and coal are white hot and the honeycombed bricks in the carburettor and superheater are a dull cherry red. This takes from two to four minutes. This is called the "blow" and is followed by the "run". The air is shut off and steam is sent through the generator. As the steam passes through the hot coke it is reduced and carbon monoxide and hydrogen are formed. The mixture of these two gases is water gas.

Since water gas has a low heating value it has to be enriched by mixing it with a gas of high heating value. In order to do this oil is sprayed into the top of the carburettor and is "cracked" or broken up into gases having a high heating value as it passes through the honeycomb of hot bricks in the carburettor and superheater. The steam passing through the hot coke in the generator cools it and after about four minutes of gas making, the fire is cooled to such an extent that the reaction fails to take place. The steam is turned off and a blast of air is again sent through the fire. This process is repeated, the blow and run alternating with each other.

The hot carburetted water gas passes from the superheater to the wash box where the gas is cooled and some of the tar removed. All of the oil used

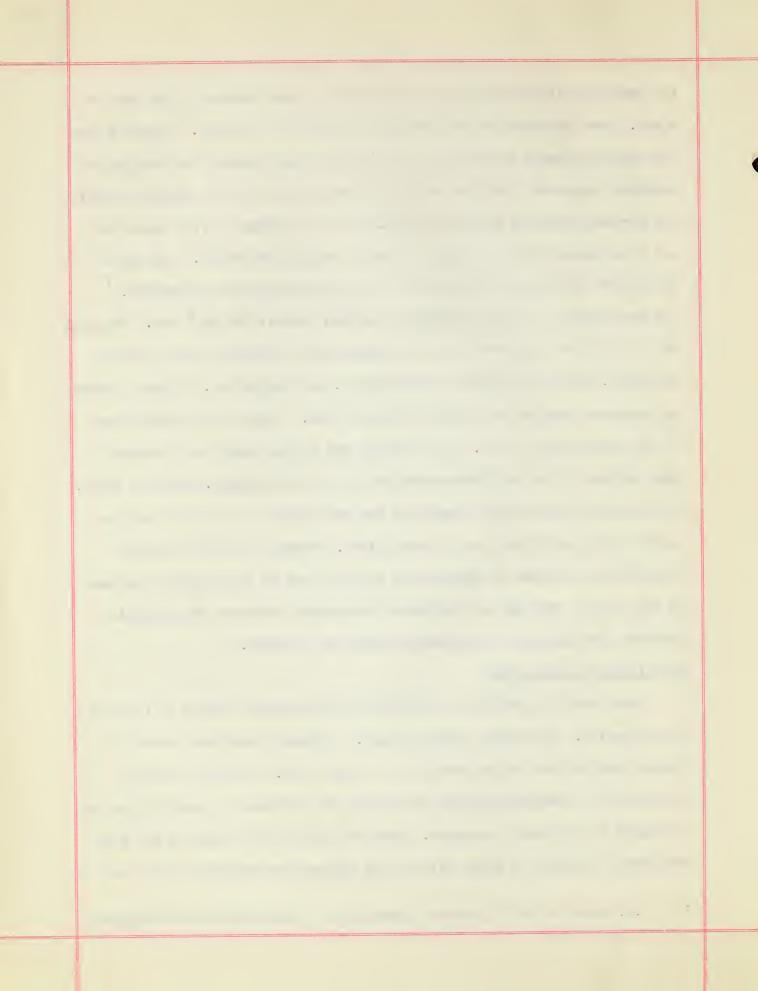


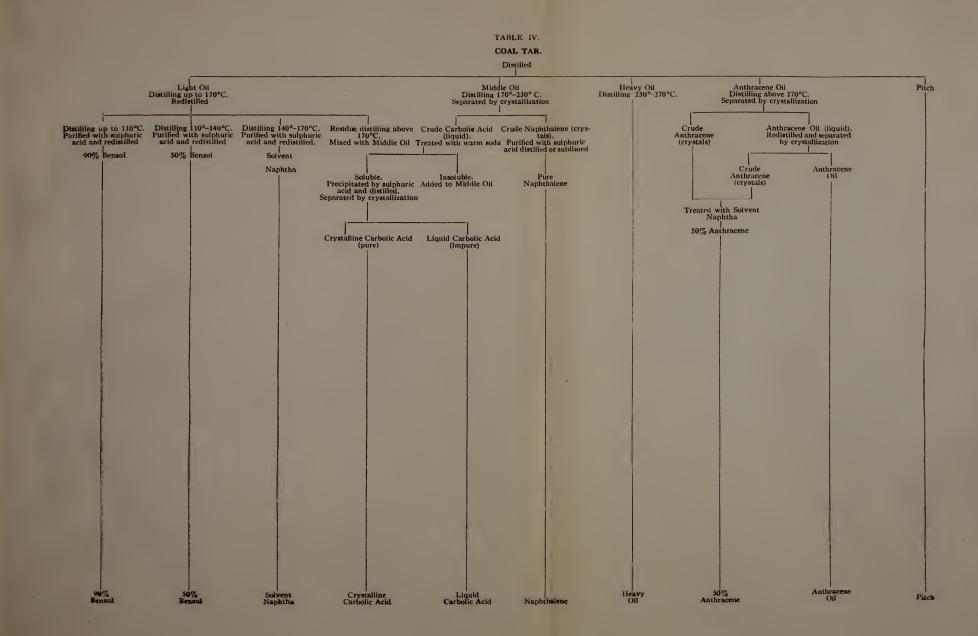
for enriching is not converted into a gas and some remains in the form of a tar. From the wash box the gas goes to the relief holder. A pump called the exhauster draws the gas from the relief holder through the cooling and scrubbing apparatus and then forces it through the purifier boxes to remove any carbon dioxide or hydrogen sulphide that is present, after which the gas is measured by being passed through a large plant meter. The gas is then stored in holders from which it can be distributed to customers. The by-products of the gas industry are coke armonia and coal tar. The coal tar is distilled and from it we get many useful substances such as "coal tar" dyes, "coal tar" drugs, disinfectants, and explosives. Figure 7 shows the numerous products obtainable from coal tar. Coke finds extensive use in the metallurgy of iron. It is porous and strong enough not to crush when covered by ore and other materials in a blast furnace. Coke is today, and has been in such great demand in the metallurgy of iron that coal was destructively distilled for the coke alone. Formerly all the volatile products were allowed to escape into the air, but at the present time much of our coke is produced in the modern by-product ovens and the volatile products are conducted away through pipes and purified.

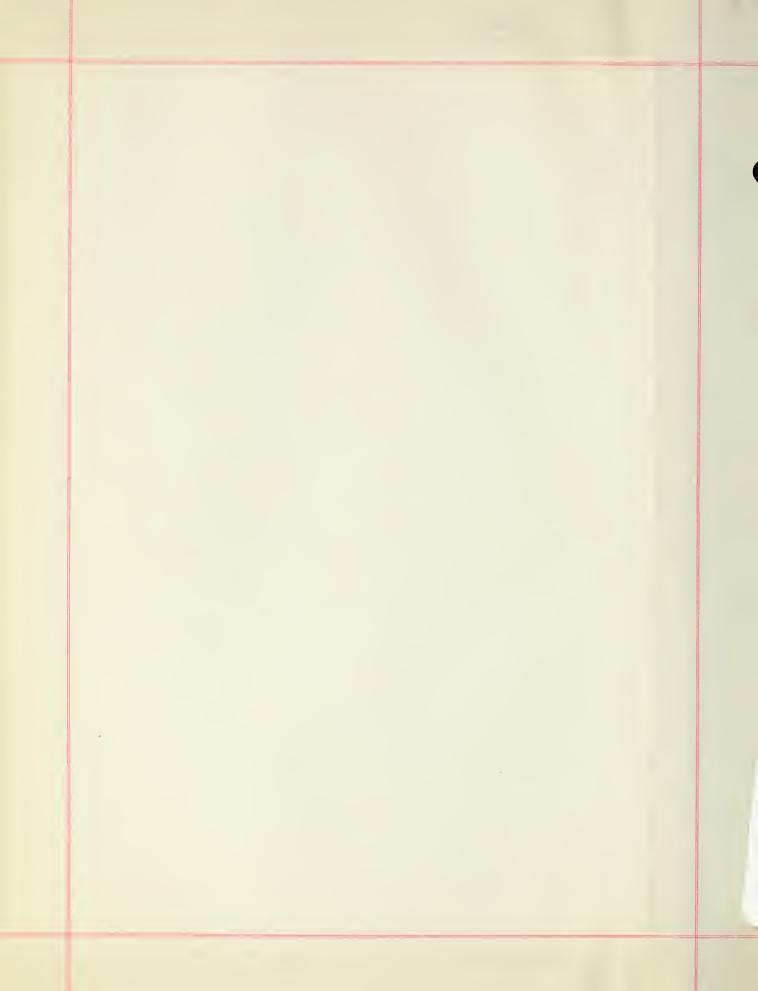
# Distillation of Coal Tar:

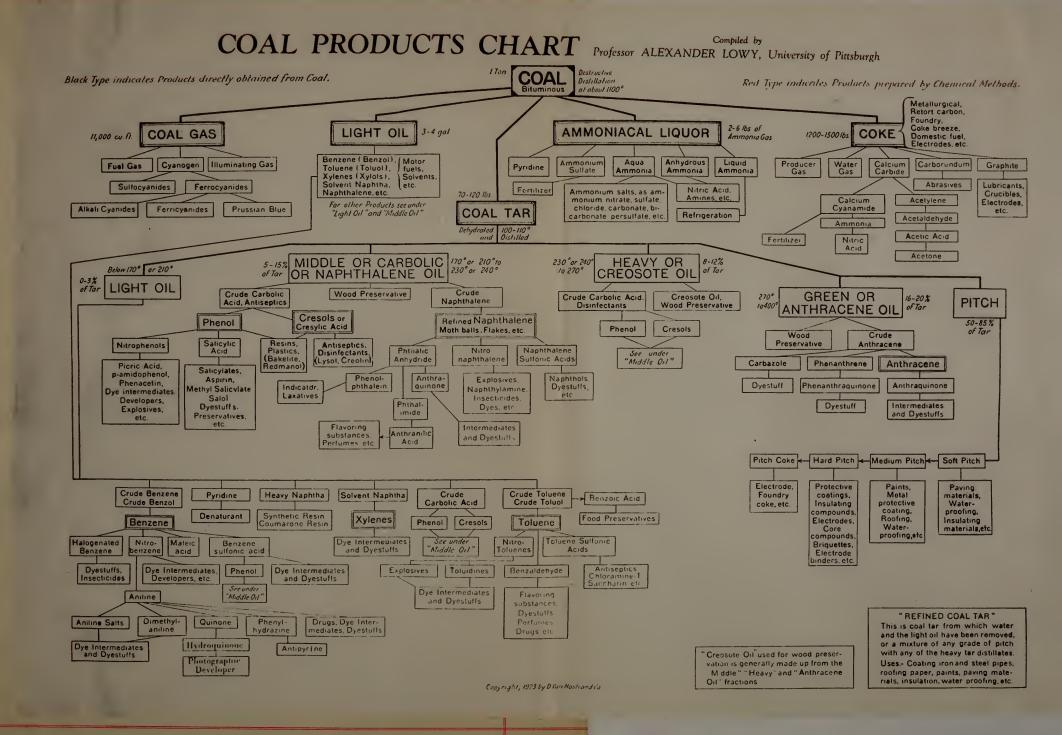
Coal tar is distilled in wrought iron cylindrical stills of 10 to 20 tons capacity. The stills stand upright. Although sometimes heated by steam, they are more often heated by a direct fire. The still head is connected to a condensing worm, from which the products of distillation are conducted to different receivers. When the distillation process has been completed, the fire is drawn out and the temperature allowed to fall to a

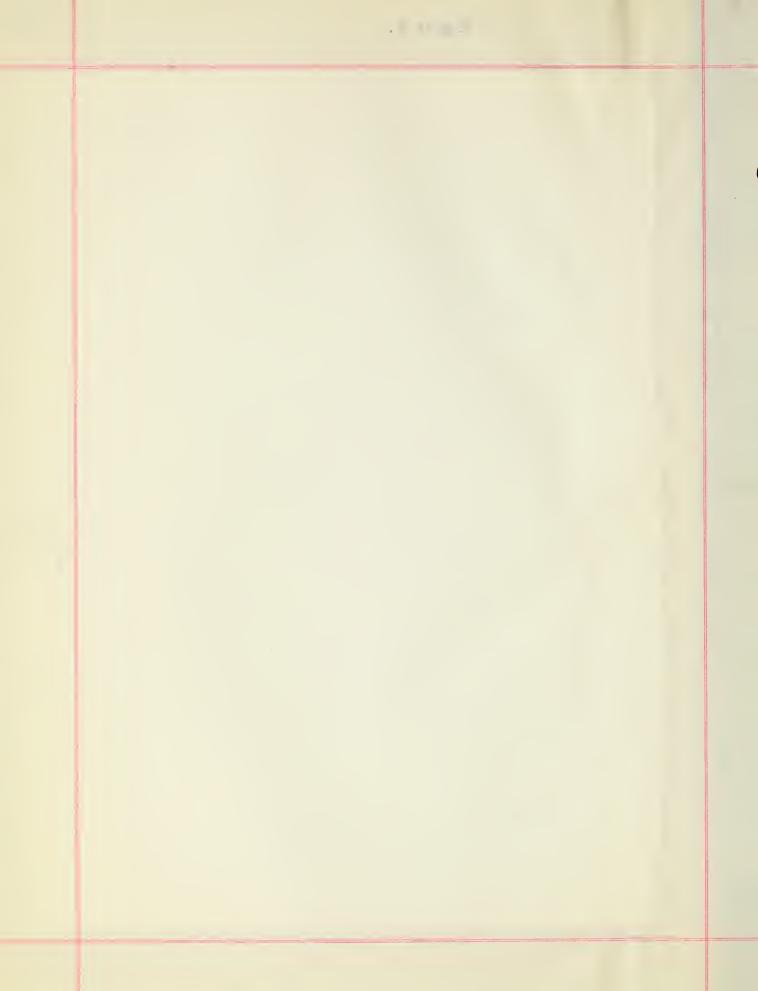
17 - W.E.Bureau of Public Service Information - Manufactured Gas (Pamphlet)











point at which the pitch in the still remains liquified but will not ignite when it comes in contact with air. The pitch is run out into barrels or other suitable receivers. The table, Figure 6, page 34, shows diagramatically the first products of a tar distillation. These products are themselves the parent substances of innumerable compounds.

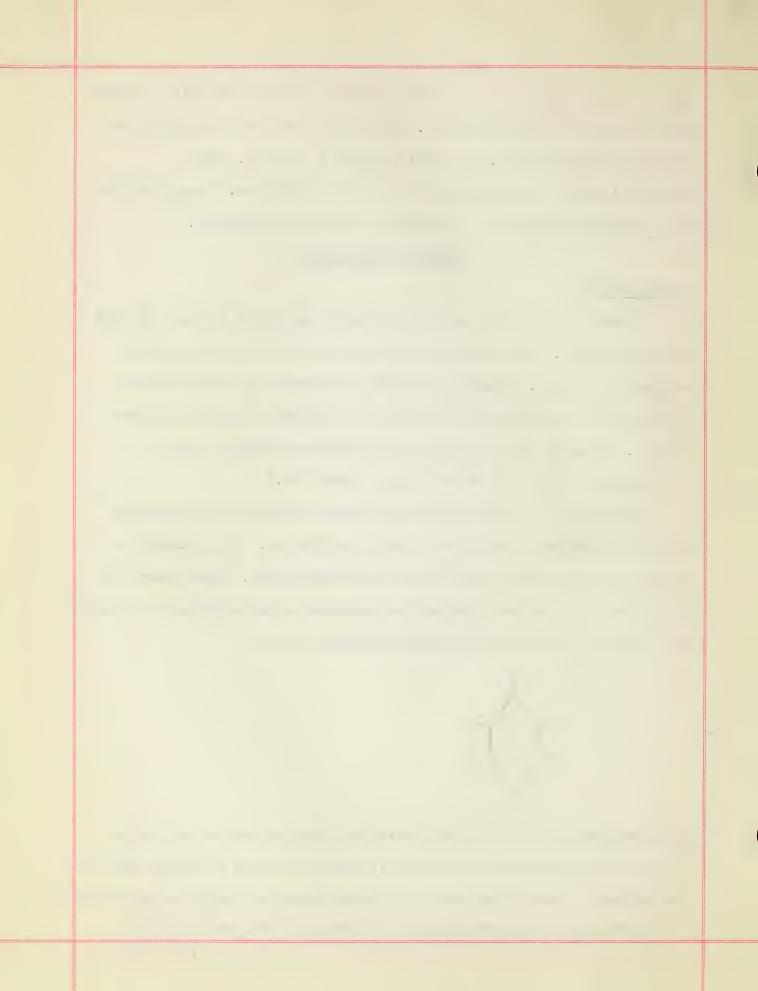
#### AROMATIC HYDROCARBONS

#### BENZENE SERIES

Benzene is the first member of a series that bears its name and has the formula  $C_6H_6$ . Care should be taken to note the difference between benzene and benzine. Benzine is one of the products of the fractional distillation of petroleum and consists of a mixture of aliphatic hydrocarbons. "Benzene and some of its homologues are products of the distillation of coal and are contained in coal tar."

The number of carbon atoms in the benzene molecule is six and the number of hydrogen atoms in the molecule is also six. It is logical to assume that each carbon atom carries one hydrogen atom. Since there are six carbon atoms and each one must be connected to its neighbor by at least one bond we may assume the structural formula to be:-

This accounts for only three of the valence bonds of the carbon, and we know from past knowledge that carbon is tetra-valent, so we assume that the 4th valence of each carbon atom is directed toward the center and not attached 5 - Remsen, Ira - An Introduction to the Study of Compounds of Carbon -



to any particular atom, thus:-

4

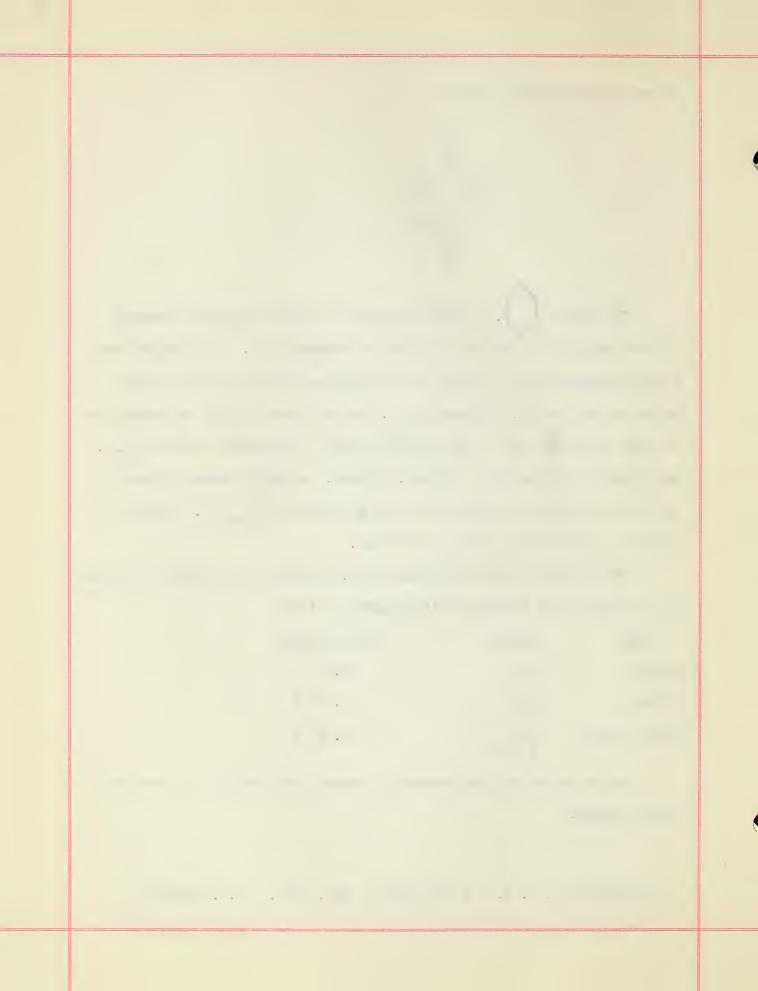
The symbol  $\bigcirc$ , a regular hexagon is used to represent benzene without any symbols for the hydrogen and carbon atoms. If we substitute a methyl group (C H  $_3$ ) for one of the hydrogen atoms, we get the next member of the series, toluence C $_7$ H $_8$ . On the other hand if we substitute an ethyl group for one of the hydrogen atoms we get ethyl benzene C $_8$ H $_1$ O $_1$ O. The aromatic hydrocarbons benzene, toluene, and ethyl benzene belong to the benzene series and answer to the type formula C H $_1$ O $_1$ O. These are products of the distillation of coal tar.

The following table gives the names, formulas and the boiling points of the first three members of the benzene series:-

Name	Formula	Boiling Point
Benzene	ce <sub>H</sub> e	80.36° C
Toluene	C H 7 8	111.00° C
Ethyl benzene	C H 8 10	136.50° C

The following are the structural symbols for benzene, toluene and ethyl benzene:-

4 - Chamberlain, J. B. - A Text-book of Org. Chem. - P.P. 444-448





H -C-H

Benzene

Toluene or methyl benzene

Ethyl benzene

7.

Benzene can be prepared by passing acetylene through a tube heated to a dull redness.

$$3 C_{22} \longrightarrow C_{66}$$

Three molecules of acetylene are converted into one molecule of benzene.

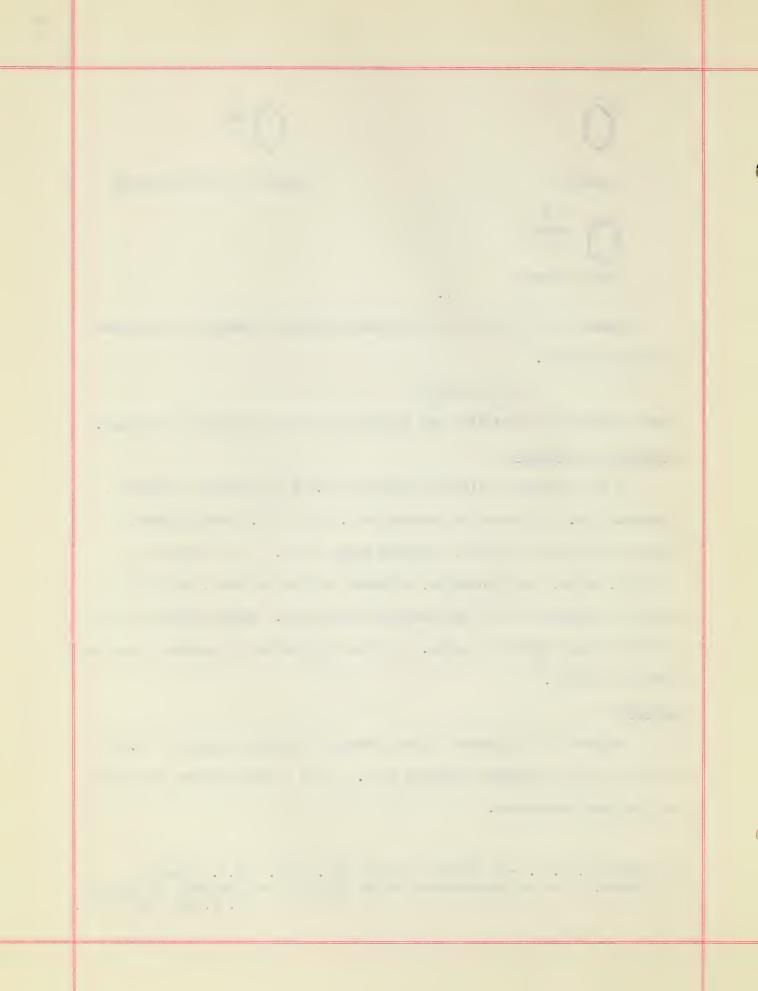
Properties of benzene:-

It is a colorless liquid boiling at 80.5°C and having a peculiar, pleasant odor. Its specific gravity is 0.899 at 0°C. When ignited, benzene burns with a bright. luminous smoky flame. It is soluble in alcohol, ether, and chloroform, slightly soluble in water, and is an excellent solvent for oil and resinous substances. Large quantities are used in making synthetic indigo. A great deal of crude benzene is used as a fuel in motors.

# Toluene: -

Toluene is a colorless liquid having a specific gravity of 0.882 at 0°C and has a pleasant aromatic odor. It is a good solvent for oily and resinous substances.

<sup>7 -</sup> Williams, R. J. - An Introduction to Org. Chem. - P.P. 363-369 5 - Remsen, Ira - An Introduction to the Study of the Compounds of Carbon P. P. 308, 309 & 311.



# Ethyl benzene:-

Ethyl benzene is a colorless liquid with an aromatic odor and having a specific gravity of 0.883 at 0 C. Like benzene and toluene, it is a good solvent for oily and resinous substances.

THE FOLLOWING CHART SHOWS THE RELATIONSHIP BETWEEN THE CLASSES OF ORGANIC COMPOUNDS DISCUSSED IN THE FOLLOWING PAGES.

ALCOHOIS: - Alcohols may be regarded as hydroxyl substitution products of hydrocarbons, thus,

Ethane

Ethyl Alcohol.

ALDEHYDES: - All aldehydes have the radical "CHO" as a distinguishing feature and are partial oxidation products of alcohols.

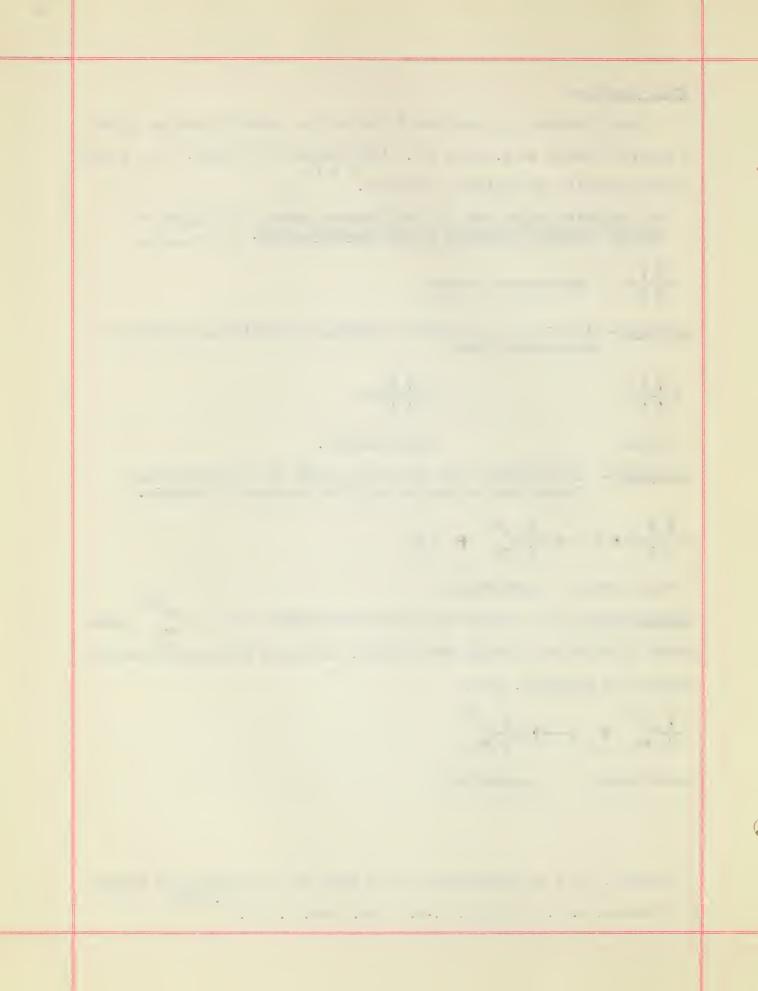
Ethyl Alcohol Acetaldehyde

ORGANIC ACIDS:- The organic acids are characterized by the which is called the carboxyl group (COOH), and may be considered oxidation products of aldehydes, thus,

$$H - \overset{H}{\overset{}_{C}} - \overset{}{\overset{}_{C}} \overset{}{\overset{}_{C}}$$

Acetaldehyde Acetic Acid

<sup>5 -</sup> Remsen, Ira - An Introduction to the Study of the Compounds of Carbon -P. 309 16 - Perkins, W. H. & Kipping, F. S. - Org. Chem. P. 371.



ESTERS:- Just as an acid and a base yield a salt and water, so an acid and an alcohol yield an ester and water.

Ethyl Alcohol

Ethyl Chloride.

ETHERS:- The ethers may be considered as derived from alcohols by replacing the hydrogen of the hydroxyl group by an organic group such as CHg or C2H5, thus

C2H5OH

C2H5-0-C2H5

Alcohol

Ether

KETONES: The ketones contain the carbonyl group (CO) which is characteristic of this class of compounds, thus,

CH<sub>3</sub>-CO-CH<sub>3</sub>

There are several classes of oxygen derivatives of the hydrocarbons.

Among them are the important compounds known as alcohols, ethers, aldehydes, and acids.

#### ALCOHOLS

## Methanol or wood alcohol:-

Alcohols may be regarded as hydroxyl substitution products of the

H
hydrocarbons. As an example H-C-H is the formula for marsh gas or

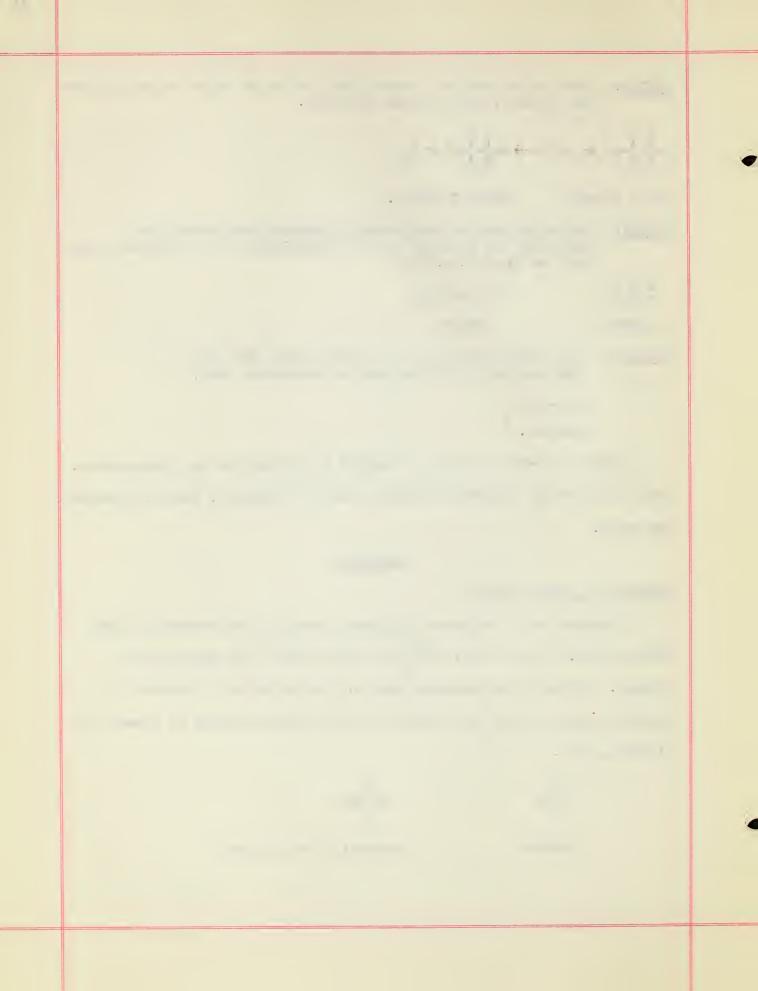
H
methane. If one of the hydrogen atoms of the molecule is replaced by a
hydroxyl group, we have the formula for the simplest member of a series of
alcohols, thus:

H H-C-H H

Н Н-С-ОН Н

Methane

Methanol or wood alcohol



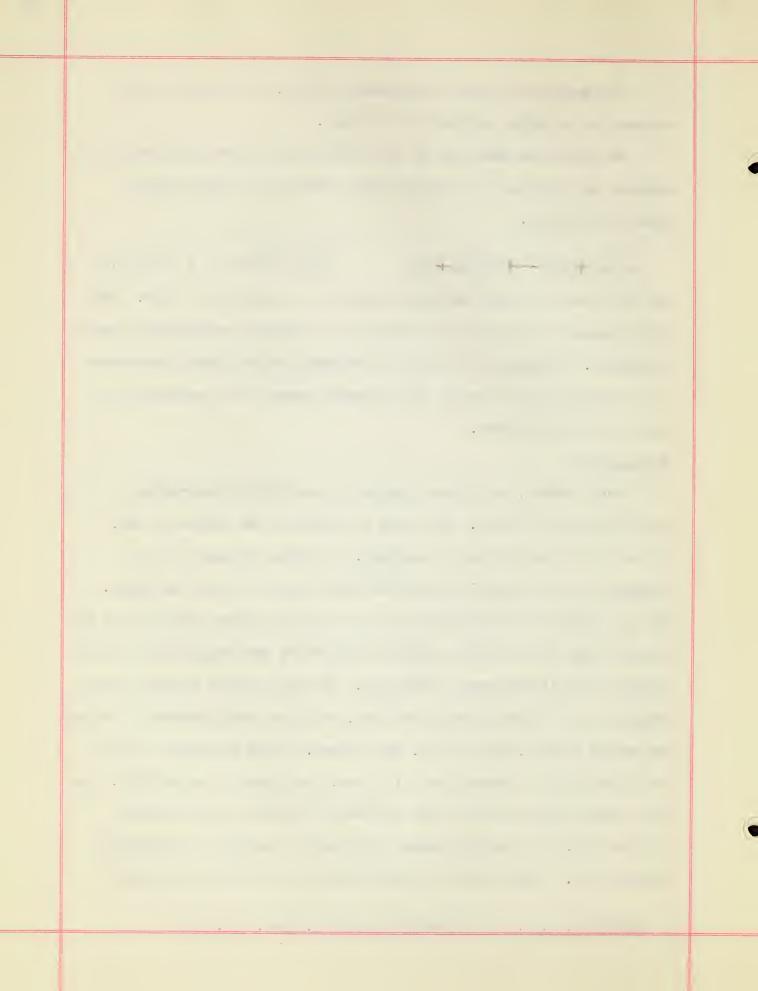
The empirical formula for methonal is  $\mathrm{CH}_4\mathrm{O}$ , or we may say that methanol is an oxygen derivative of methane.

We can obtain some idea of the arrangement of atoms in molecules of methanol by observing the reaction which takes place between methyl chloride and water.

#### Wood Alcohol:-

Wood alcohol, as the name implies is made by the destructive distillation of dry wood. When wood is heated in the absence of air, carbon is left in the form of charcoal. The other products of the decomposition are volatile substances consisting of liquids and gases. The gases consist of hydrocarbons and the liquid portion consists of a low boiling light liquid of acid character (known as wood spirits) and a high boiling thick liquid known as wood tar. The wood spirits contain several compounds in the form of water solution, the three most important of which are methyl alcohol, acetic acid, and acetone. After the acetic acid in the light liquid is neutralized with lime, the liquid is redistilled. The lime reacts with the acetic acid and holds it back as a non-volatile calcium salt, while methyl alcohol with some of the other constituents distils over. After water has been added to the distillate in order to

7 - Williams, R. J. - An Introduction to Org. Chem. - P. 63



separate out some of the oily hydrocarbons the solution is again distilled. This last distillation takes place in a tall still known as a column still in which the liquid undergoes fractionation and a distillate is obtained containing a high percent of methyl alcohol. The best product obtained in this manner is known as "columbian spirits" and contains about 95% of methyl alcohol, the remainder being water and traces of other compounds.

Synthetic methanol:-

Recently a synthetic method for making methyl alcohol on a commercial scale has been developed and seems likely to replace the old method of wood distillation. In this process carbon monoxide and hydrogen are made to react under pressure in the presence of a catalyst to form methanol.

Since water gas is composed mostly of carbon monoxide and hydrogen, the crude materials for the industrial operation of this synthesis are easily available and the process is a successful one.

Methanol has also been made on an industrial scale by a similar catalytic reaction of carbon dioxide and hydrogen according to the following equation:-

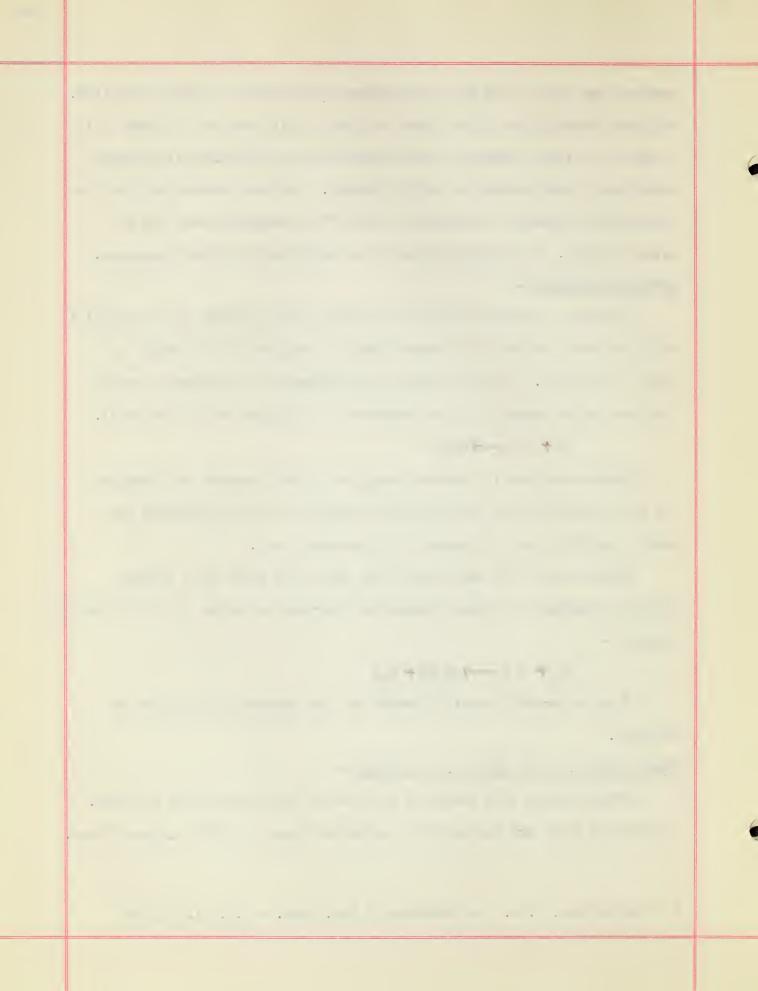
This is another practical method for the synthetic production of 4 methanol.

# Ethyl alcohol, grain alcohol, or ethanol:-

Ethyl alcohol is a substance produced by the fermentation of sugar.

In practice there are two possible sources of sugar for this purpose: first,

4 - Chamberlain, J. S. - A Text-book of Org. Chem. - P.P. 91, 22 & 93



plants naturally containing sugar ready to be converted into alcohol by simple fermentation and second, materials containing starch which may be changed into sugar by the action of malt or acids and then fermented.

Potatoes and grain come under the latter class. A new process for making alcohol from sawdust has recently been developed. (see page 76).

Yeast, which is a low form of plant life contains several enzymes, one of which (zymase) acts as a catalytic agent in the preparation of alcohol by the fermentation of sugar. When yeast is placed in a sugar solution and the mixture allowed to set the following reaction takes place:-

$$C_{6}H_{12}O_{6} \longrightarrow 2 C_{2}H_{0}H + 2 CO_{2}$$
sugar alcohol carbon dioxide

The alcohol formed is separated from the rest of the solution by 19 fractional distillation.

Commercial alcohol manufactured from grain or potatoes (materials which contain starch) is made by a process which divides itself into two stages, (1) brewing and (2) distilling.

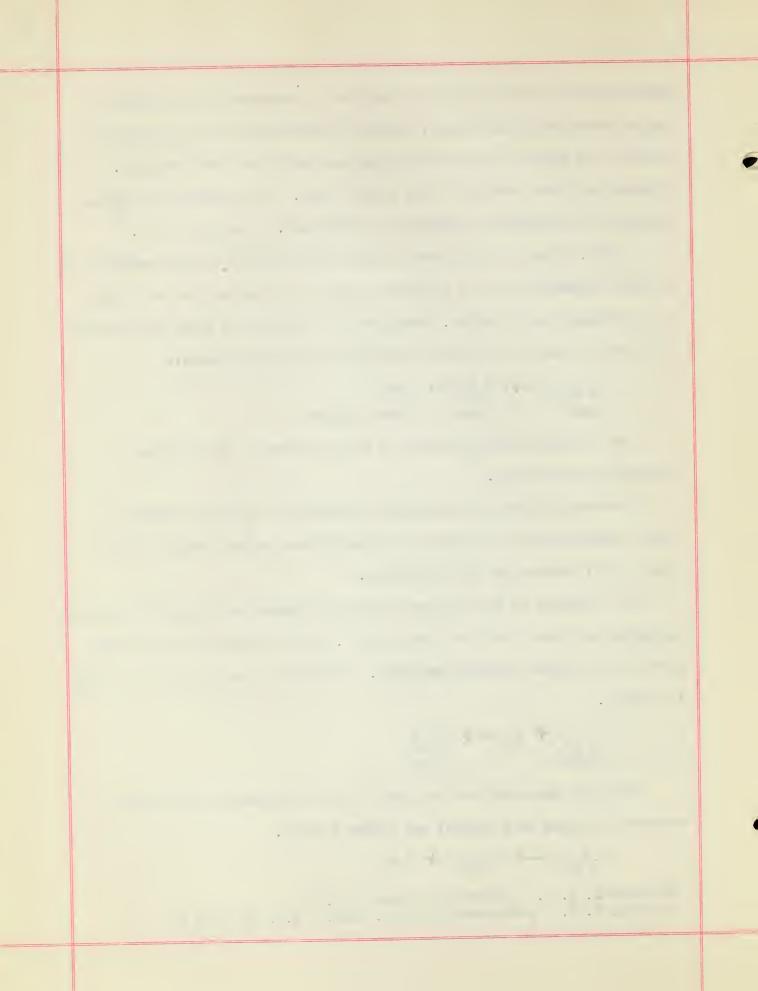
(1) Brewing is the process by which the starch in the grain is first converted into sugar and then into alcohol. By the action of malt (which contains the enzyme diastase) on grain, the starch in the grain is converted into sugar.

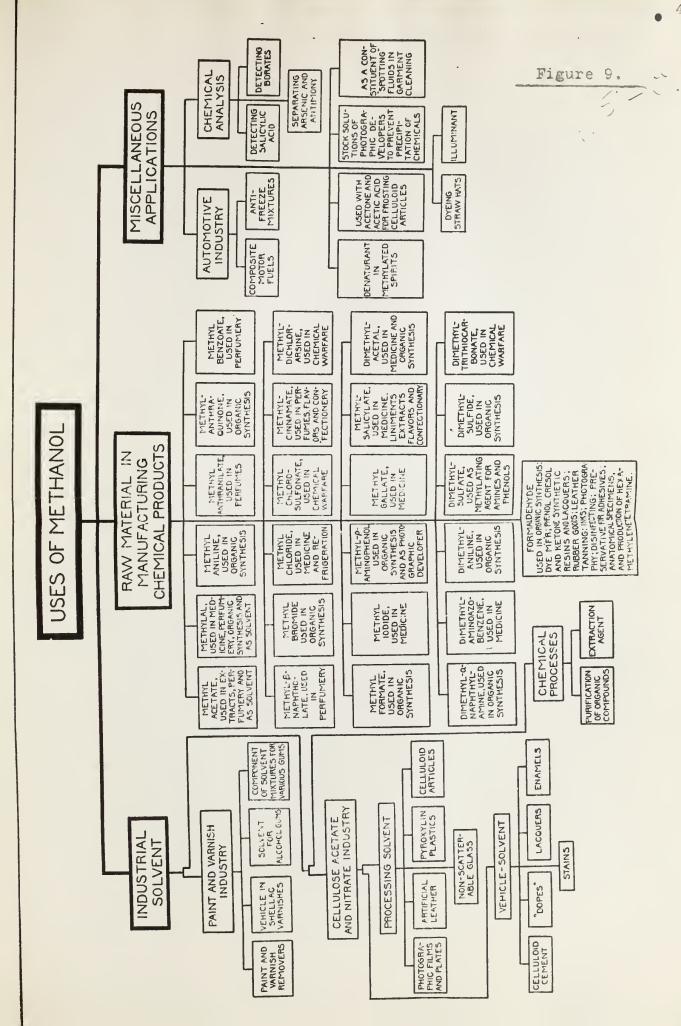
$$\begin{array}{cccc}
C & H & O & + & H & O & \longrightarrow & C & H & O \\
6 & 10 & 5 & & 2 & & 6 & 12 & 6
\end{array}$$
starch sugar

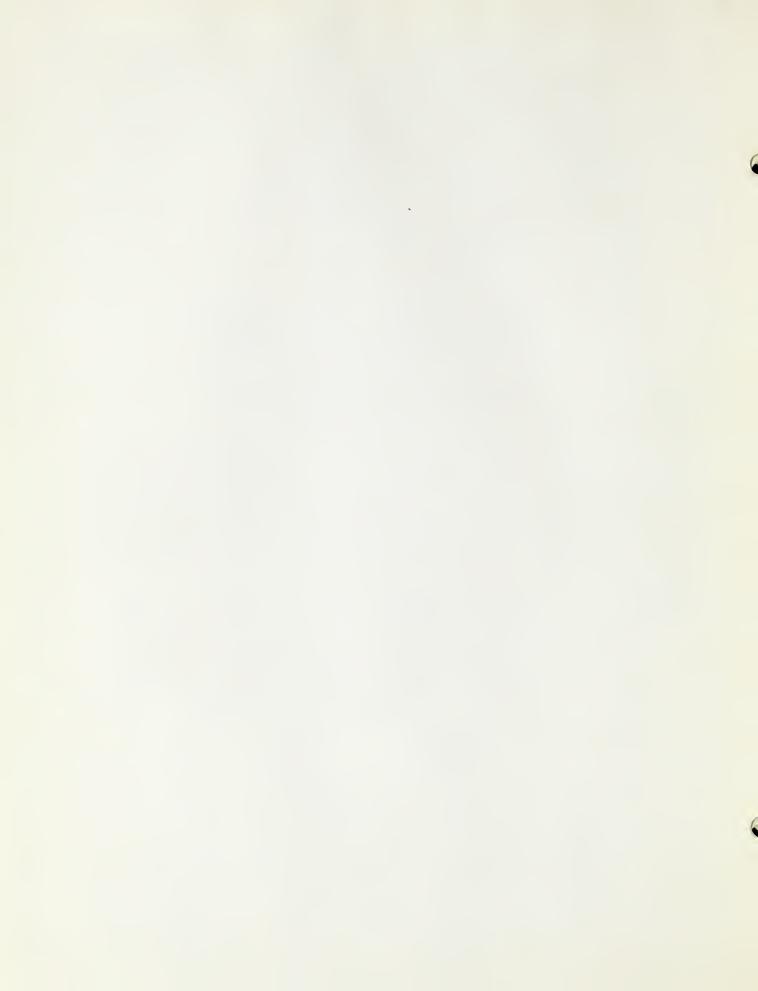
Yeast is then added and the enzyme zymase, present in the yeast, converts the sugar into alcohol and carbon dioxide.

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

18-McIntosh, J. G. - Industrial Alcohol - P. 65 19-Cohen, J. B. - A Class-book of Org. Chem. - P.P. 21, 22 & 23







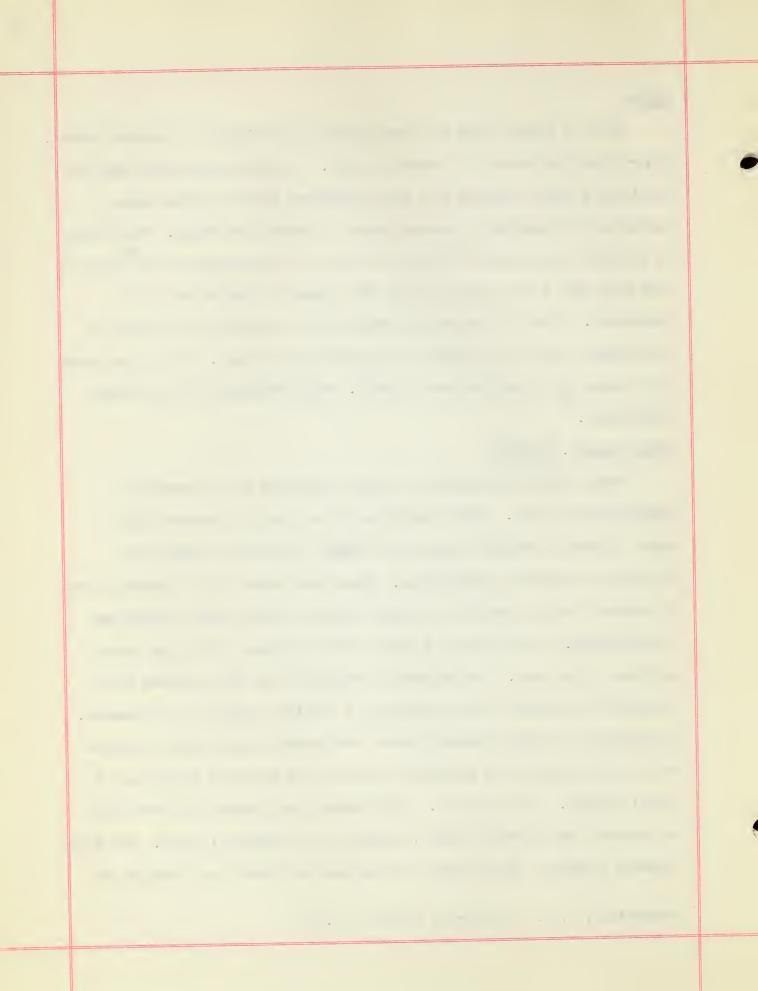
#### Malt:-

Malt is barley which has been allowed to germinate to a certain extent, after which the process is stopped by heat. In germinating grain there is developed a small quantity of a white substance called diastase which possesses the property of causing starch to change into sugar. The barley is steeped in cold water for about 50 hours at a temperature of 15°C and is then made into a heap upon the malt floor where it remains until it germinates. Oxidation causes its temperature to increase and it must be occasionally turned to prevent it from becoming too warm. It is then dried at a temperature slowly raised to 150°F. This temperature stops further 18 germination.

## Butyl alcohol, butanol:-

Butyl alcohol is produced in large quantities by the bacterial fermentation of corn. After the starch of the corn is converted into sugar (glucose), butanol together with ethyl alcohol and acctone are obtained by bacterial fermentation. Along with these liquid products there is obtained large quantities of a gas composed of 60% carbon dioxide and 40% hydrogen. This gas was at first a waste product, but is now being utilized in two ways. The hydrogen is separated and then combined with atmospheric nitrogen in the presence of a catalytic agent to form ammonia. The hydrogen can also be used to react with carbon dioxide under pressure and in the presence of a catalytic agent for the synthetic production of methyl alcohol. (see page 43). This fermentation process has been used to produce a new solvent alcohol, butanol, on a commercial scale. Two other valuable solvents, ethyl alcohol and acetone are formed, and from the by-

18-McIntosh, J. G. - Industrial Alcohol - P. 63



To face rage 58]



product gases, both ammonia and methyl alcohol can be synthesized. The discovery of methods for the commercial production of butanol, ethanol, methanol and acetone are responsible for the development and perfection of nitro-cellulose lacquers used for automobile finishing and in air plane 4 construction.

The following table give the names, formulas, boiling points, and specific gravities of a number of alcohols:-

Phecrite Strat	0100 01 00 11011001	01 0100110110	Boiling	Specific
Common name	Official name	Formula	Point	Gravity
Methyl Alcohol	Methanol	CH <sub>3</sub> OH	64.5 C	0.792
Ethyl Alcohol	Ethanol	С <sub>2</sub> Н <sub>5</sub> ОН	78.5°C	0.789
Propyl Alcohol	.Propanol	C <sub>3</sub> H <sub>7</sub> OH	97.8°C	0.804
Butyl Alcohol	Butanol	C <sub>4</sub> H <sub>9</sub> OH	117.7°C	0.810
Amyl or Pentyl Alcohol	Pentanol	с <sub>5</sub> н <sub>1</sub> рн	137.9°C	0.817

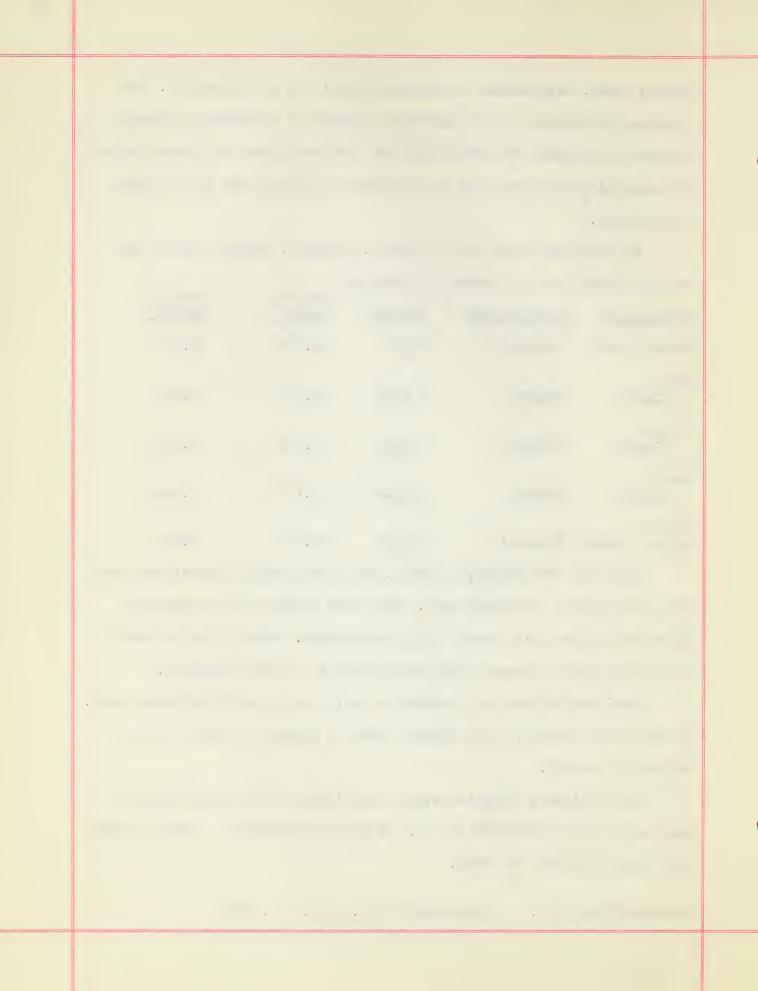
The first three members, methyl, ethyl and propyl alcohols are color-less liquids with a pleasant odor. They burn readily with a colorless flame and will mix with water in all proportions. As we go up the series the boiling point increases and the solubility in water decreases.

Butyl alcohol and amyl alcohol are oily liquids with unpleasant odor.

Of these two alcohols, butyl alcohol alone is soluble in water to any
appreciable extent.

Methyl alcohol resembles ethyl alcohol very much in appearance and odor and is easily mistaken for it. When taken internally, methyl alcohol may cause blindness and death.

4-Chamberlain, J. S. - A text-book of Org. Chem. - P. 100



When ethyl alcohol is obtained from fermented liquids by distillation, it contains water and a mixture of other higher alcohols called "fusel oil". The fusel oil may be removed in part by fractional distillation.

Fusel oil contains a mixture of propyl alcohol, butyl alcohol, and amyl alcohol. Where alcohol is to be used internally it is desirable to remove the fusel oil containing the higher alcohols as these alcohols are 4 poisonous when taken internally.

#### OXIDATION OF ORGANIC COMPOUNDS

Complete oxidation of organic compounds results in the formation of carbonic acid which is unstable and breaks down into carbon dioxide and water. However by incomplete oxidation of many organic compounds, aldehydes and stable acids are formed. This can often be accomplished by use of a suitable catalytic agent and proper conditions for the partial oxidation to take place. The partial oxidation products of methane and ethane are as follows:-

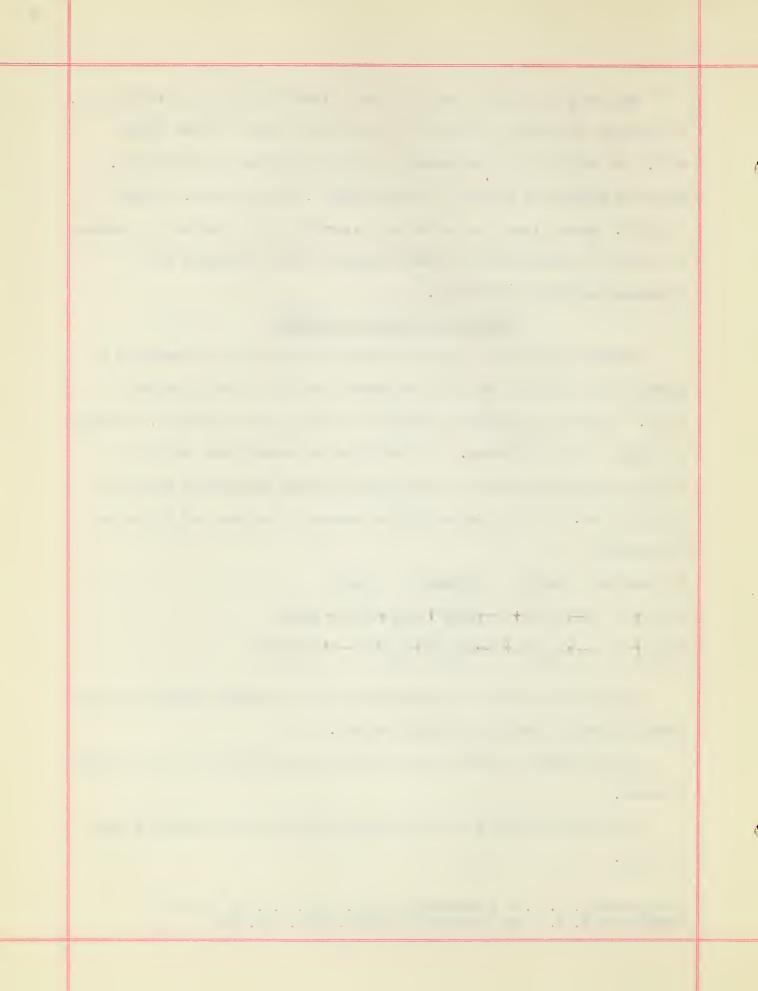
Hydrocarbon Alcohol Aldehyde Acid  $CH_4 + 0 \longrightarrow CH_3OH + 0 \longrightarrow HCHO + H_2O + 0 \longrightarrow HCOOH$   $CH_4 + 0 \longrightarrow CH_3OH + 0 \longrightarrow CH_3CHO + H_2O + 0 \longrightarrow CH_3COOH$ 

In the first step of the oxidation an atom of oxygen combines with an atom of hydrogen forming a hydroxyl radical.

In the second step two atoms of hydrogen are removed by being oxidized to water.

In the third step an atom of oxygen is added to the aldehyde forming the acid.

4-Chamberlain, J. S. - A Text-book of Org. Chem. P.P. 82, 90 & 99 7-Williams, R. J. - An Introduction to Org. Chem. - P. 108



The "OH" radical is characteristic of a group of compounds called alcohols. Alcohols differ from bases in that they do not ionize in solution or turn red lithus paper blue.

The "CHO" radical is characteristic of a group of compounds called aldehydes.

The "COOH" radical is called the carboxyl radical and is characteristic of a group of compounds known as organic acids.

#### ALDEHYDES

All aldehydes have the radical "CHO" as a distinguishing feature and are partial oxidation products of alcohols. With further oxidation they yield acids. Their names are derived from the names of the acids to which they are related, for example:-

Methyl alcohol Formaldehyde Formic acid

Ethyl alcohol Acetaldehyde Acetic acid

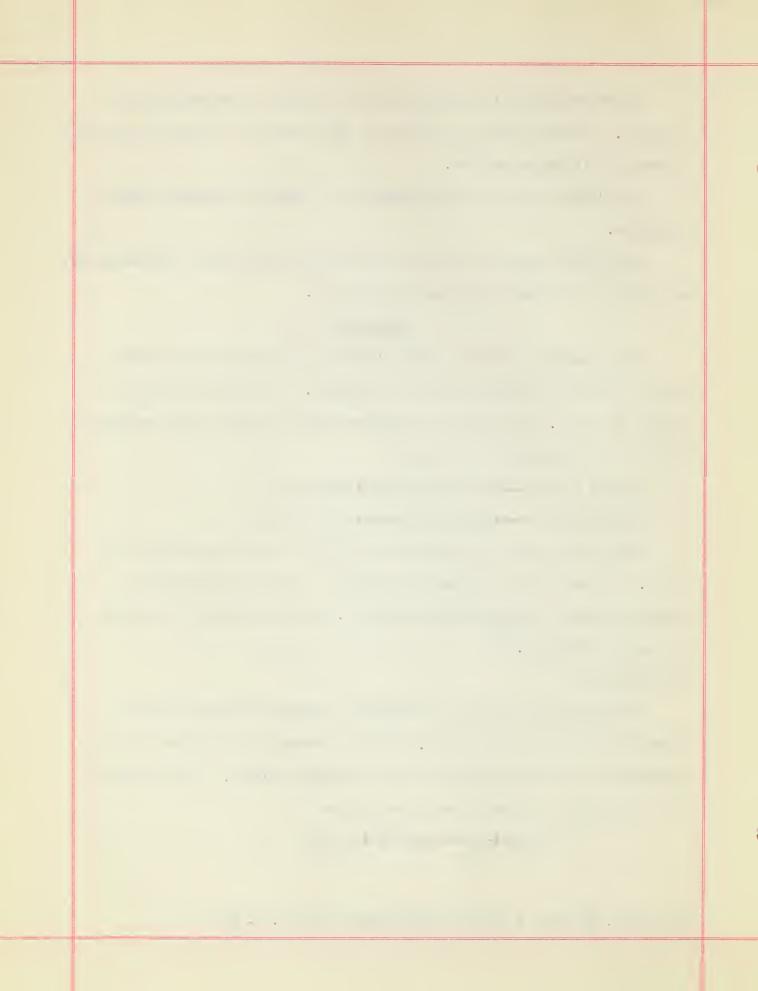
When methyl and ethyl alcohol are oxidized they are converted into acids. By proper regulation of the oxidation, products intermediate between alcohols and acids can be obtained. These intermediate products 20 are called aldehydes.

Formaldehyde:-

Formaldehyde is prepared by passing a mixture of methyl alcohol vapor and air over heated copper. After the reaction is started the heat generated by it is sufficient to keep the copper glowing. This reaction as we said before is one of oxidation thus:-

2 CH OH + 0 
$$\longrightarrow$$
 2 HCHO + 2 H O

20 - Gray, Sandifor & Hanna - Fundamentals of Chem. P. 503



A large number of metallic oxides act as oxidation catalysts, some being stronger in this respect than others. Aldehydes have recently been made by the oxidation of alcohols using certain metallic oxides as catalytic agents. Formaldehyde was made in this manner as follows:-

A mixture of dry air and methyl alcohol vapor was passed over a heated catalytic agent composed of a mixture of samarium oxide (Sm<sub>2</sub>0<sub>3</sub>) and copper oxide (CuO). The catalyst was heated to about 350°C. The heat of the reaction was sufficient to keep the catalyst at a red heat after the reaction had once started. The best yield was obtained under the following conditions:-

Temperature of the alcohol-air mixture entering the catalytic chember. 40°C

Temperature of the catalyst. 525°C

Catalytic agent:-

Sanarium oxide. 1% Copper oxide. 99%

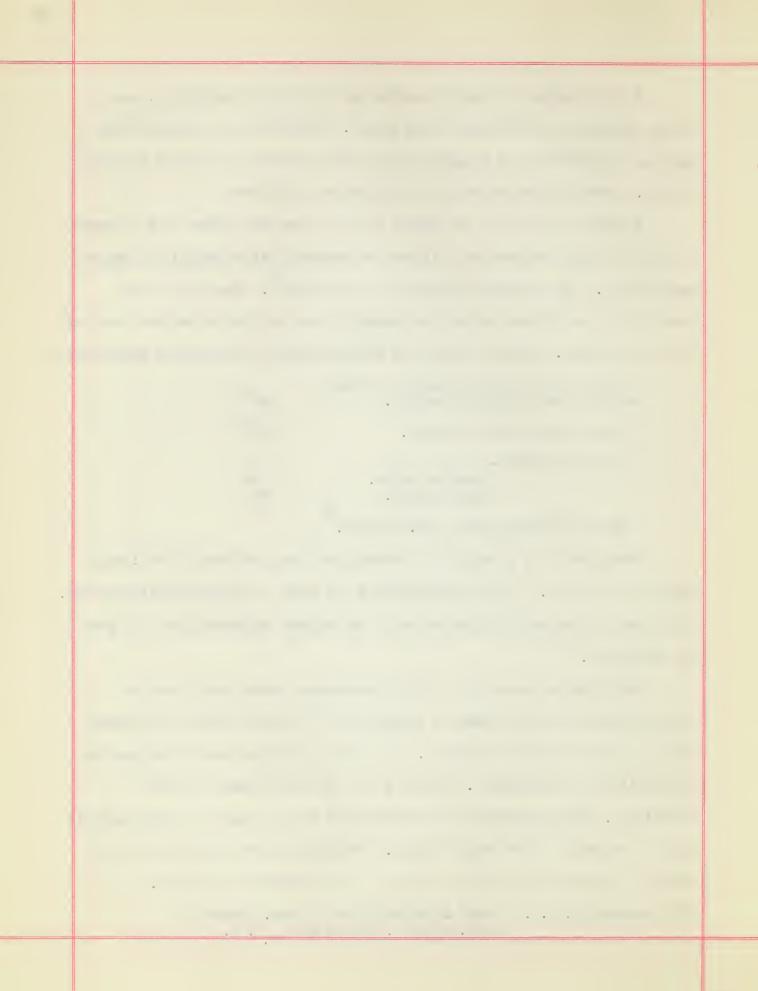
21

These conditions gave a 63.5% yield.

Formaldehyde is a gas with a choking odor and produces an irritating effect on the eyes. It is very poisonous and makes an excellent disinfectant. It is sold principally in the form of a 40% aqueous solution under the name of "formalin".

Formaldehyde reacts with protein substances making them tough and insoluble and for this reason it is used for the preservation of specimens for study, and also for embalming. Any protein material can be hardened by treatment with formaldehyde. Casein can be converted into an ivory substitute. Large quantities of formaldehyde are now used in making bakelite by its combination with carbolic acid. Bakelite is hard and tough, can be moulded into any desired shape, and is a good electrical insulator.

21 - Lowdermilk, F.R. - Vapor Phase Oxidation of Org. Compounds - Univ. of Penn. Thesis 1930 - P. 1.



#### Acetaldehyde: -

Acetaldehyde is made from ethyl alcohol by oxidation just as

formaldehyde is made from methyl alcohol by oxidation. It is much less

poisonous than formaldehyde and consequently is not used as a disinfectant.

It is not active enough to be of use in making artificial ivory or bakelite.

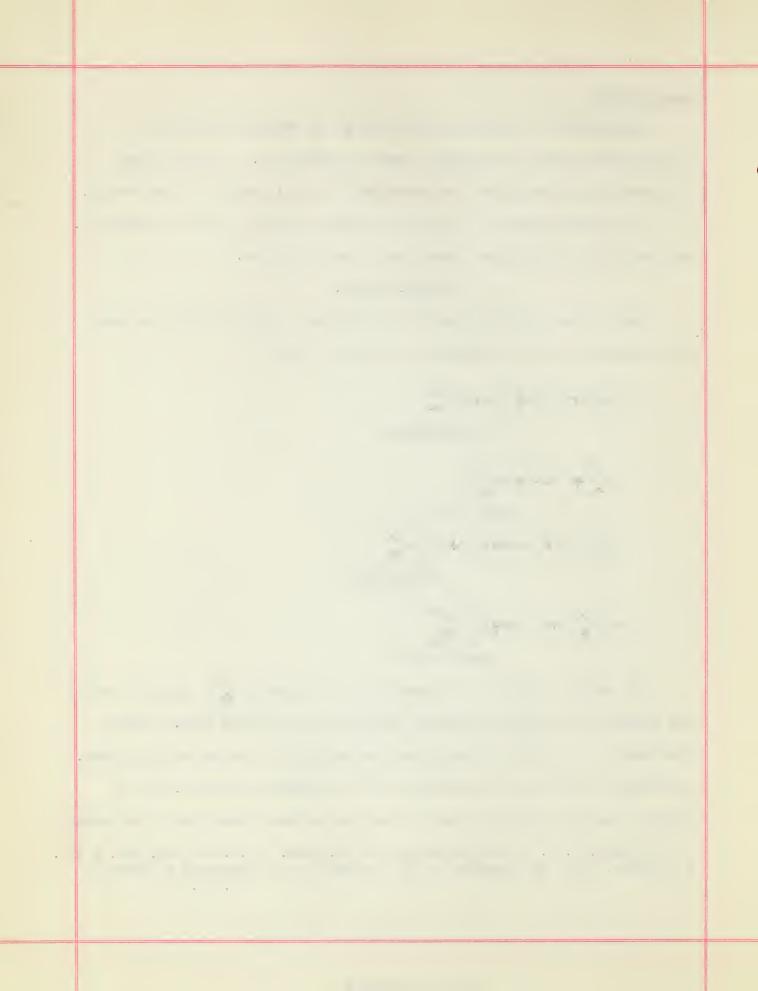
7

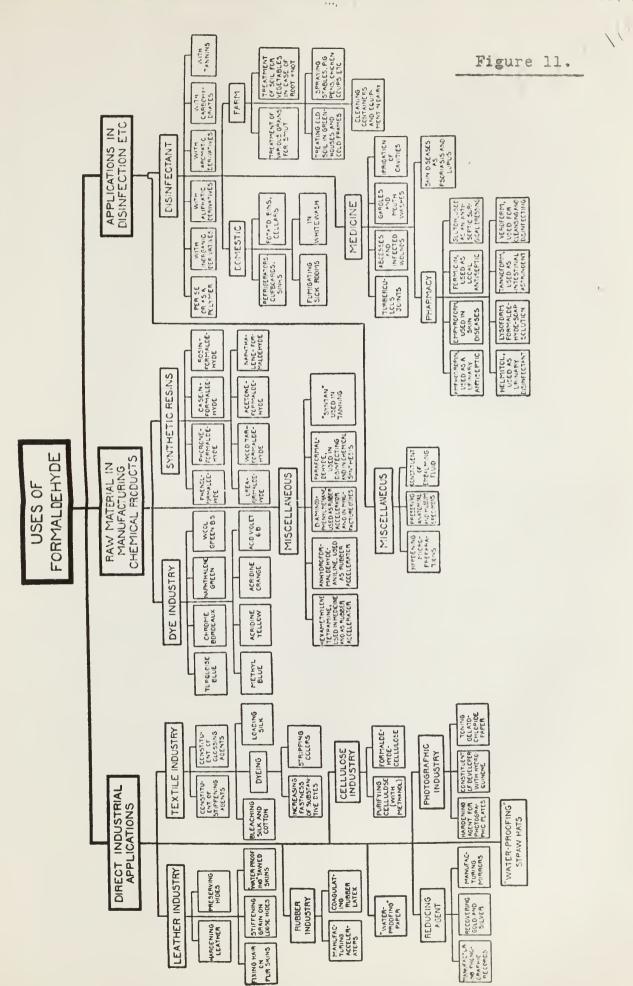
Compared with formaldehyde, acetaldehyde has little use.

## Organic Acids.

When methyl and ethyl alcohols are oxidized they are first converted 5 into aldehydes, and then oxidized into acids, thus:-

The organic acids are characterized by the group of which is called the carboxyl group and is sometimes written in this manner COOH. In the structure of the molecule the hydrocarbon radicals are joined to this group. In mineral acids all of the hydrogen may be replaced by a metal, but in organic acids it is only the hydrogen of the carboxyl group that is replaceable 7 - Williams, R. J. - An Introduction to Org. Chem. - P.P. 85, 108, 109, & 110. 5 - Remsen, Ira - An Introduction to the Study of the Compounds of Carbon - P. 54.





7

by metals. Therefore, in solution, it is the hydrogen of this group that yields the hydrogen ions. The formulas of acids are usually written so as to show the carboxyl group, but sometimes they are written with the replaceable hydrogen atoms at the beginning of the formulas.

The following table gives the names, formulas, melting points and boiling points of a few acids.

Name	Formula	Melting Point	Boiling Point
Formic	нсоон	8.6°C	100.8°C
Acetic	СН_СООН	16.7°C	118.1°C
Propionic	с н соон	-22. °C	140.7°C
Butyric	с н соон 3 7	- 7.9°C	162.5°C
Palmitic	C <sub>15</sub> H <sub>31</sub> COOH	62.6°C	Decomposed
Oleic	C H COOH	14. °C	79
Stearic	17 35 С H СООН	69.3°C	ef

# Formic acid:

This acid occurs in nature in red ants and is named after them, the latin for ants being "formicae". The sting of the ant is probably due to formic acid. It can be obtained by macerating ants with water and distilling.

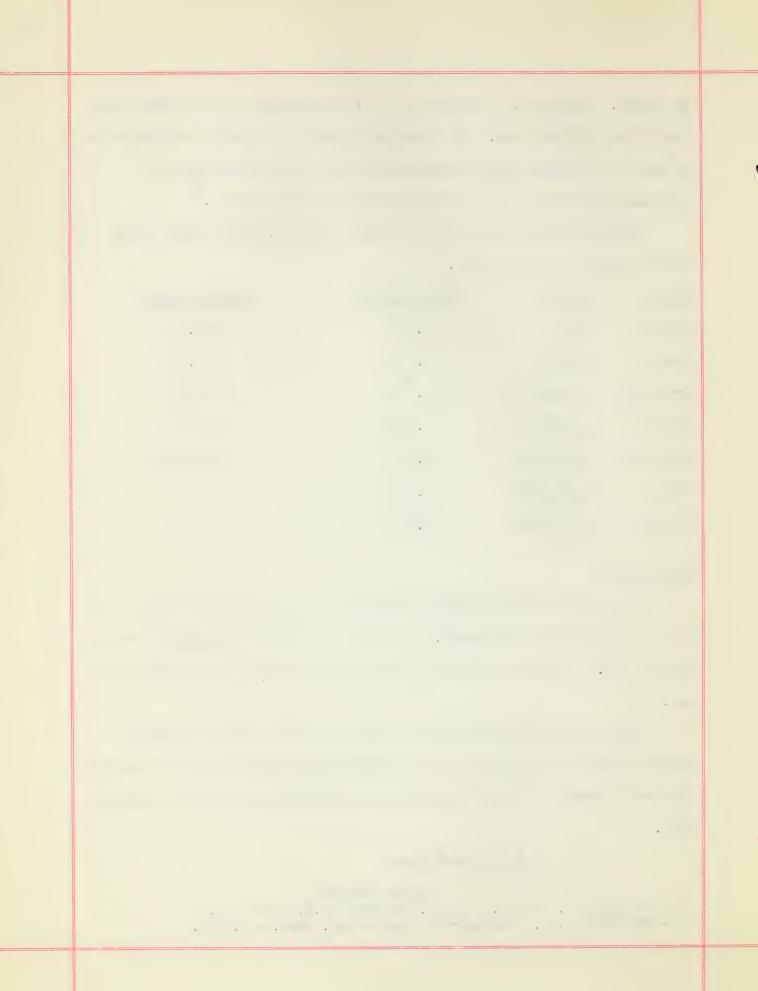
When solid sodium hydroxide is heated to 120 - 130 with carbon monoxide under a pressure of 6 to 8 atmospheres, sodium formate is produced from which formic acid may be obtained by distilling with dilute sulphuric acid.

#### CO + NaOH --- HCOONa

sodium formate

<sup>2 -</sup> Dinsmore, E. - Chem. for Sec. Schools - P.P. 334 & 335.

<sup>7 -</sup> Williams, R. J. - An Introduction to Org. Chem. - P. 125.



2 HCOONa + H SO 
$$\longrightarrow$$
 2 HCOOH + Na SO  $\stackrel{?}{2}$  4

Formic acid

Formic acid is a colorless liquid, with a pungent irritating odor.

5
It produces blisters when dropped on the skin and is a powerful antiseptic.

Acetic acid (CH<sub>3</sub>COOH):-

Acetic acid is obtained by the destructive distillation of wood and by the oxidation of ethyl alcohol.

The preparation of acetic acid from wood distillation is described to some extent under the preparation of methyl alcohol (page 42). The light distillate known as wood spirits contains between 4 and 8 percent of pure acetic acid which can be separated by converting into the calcium salt or sodium salt. This is done by treating the wood spirits with lime. The calcium acetate which is formed is then treated with sulphuric acid and distilled.

2 
$$CH_3COOH + CaO \longrightarrow H_2O + Ca(CH_3COO)_2$$
Calcium acetate

The formula for calcium acetate may also be written

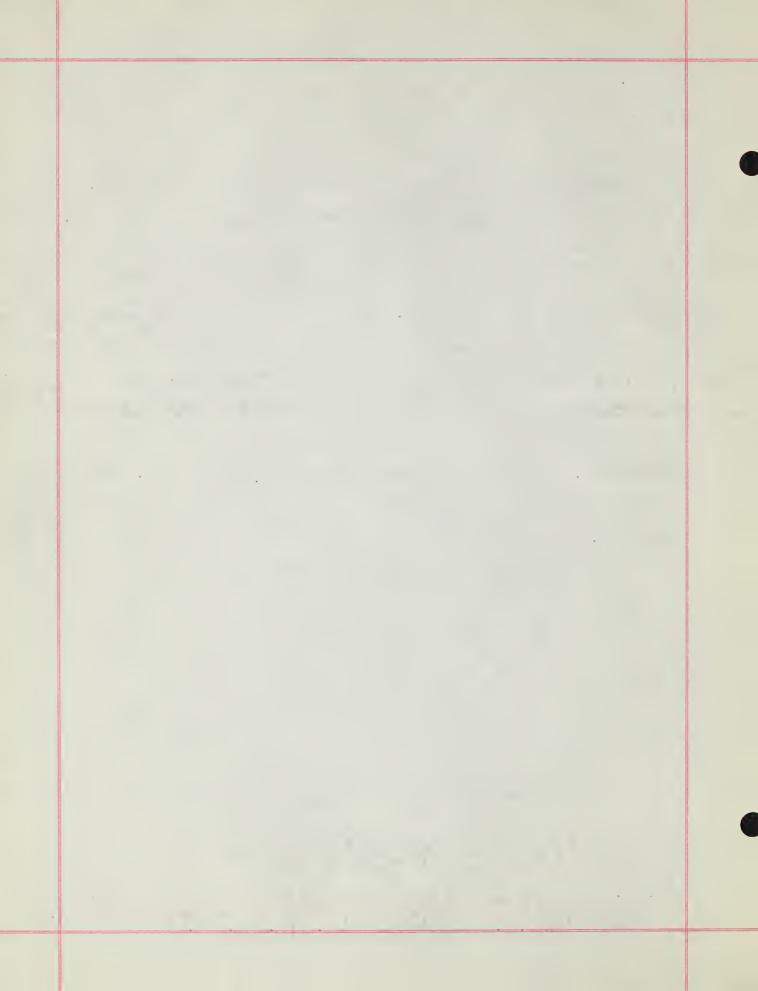
$$c_{H_3}c_{00}$$
 $c_{H_3}c_{00}$ 
 $c_{A_3}c_{00}$ 
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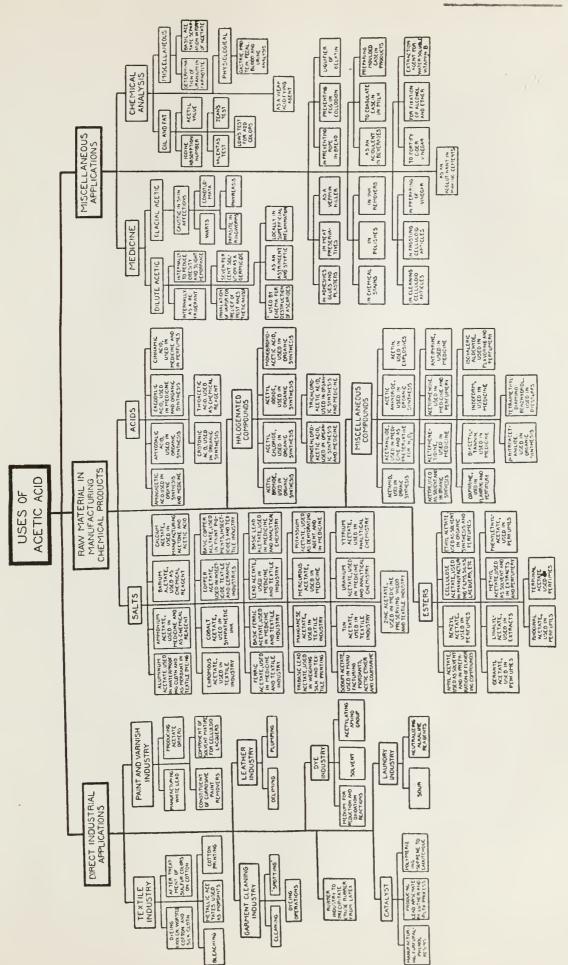
Pure acetic acid is a colorless crystalline solid which melts at

16.7 C. It is miscible with water alcohol and ether in all proportions.

5 - Remsen, Ira - An Introduction to the Study of the Compounds of Carbon -P.56

4 - Chamberlain, J. S. - A Text-book of Org. Chem. - P. 136.







Vinegar is dilute acetic acid. The acetic acid in vinegar is produced by the oxidation of ethyl alcohol contained in "hard" cider. When hard cider is left exposed to air, it soon becomes sour, the alcohol which it contains being converted into acetic acid. This change is one of oxidation brought about by a microscopic organism (Bacterium Aceti) which gets into the solution from the air.

In the "quick vinegar process" which is much used in the manufacture of vinegar, large vats filled with wood shavings are employed. The shavings are first moistened with vinegar in order that they may become coated with a growth of the ferment. Dilute alcohol is then allowed to trickle over the wood shavings in contact with the ferment and with air admitted near the bottom of the vats. In this way the alcohol is oxidized into acetic acid. The dilute acetic acid formed is "vinegar".

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$$

Propionic acid (C H COOH):-

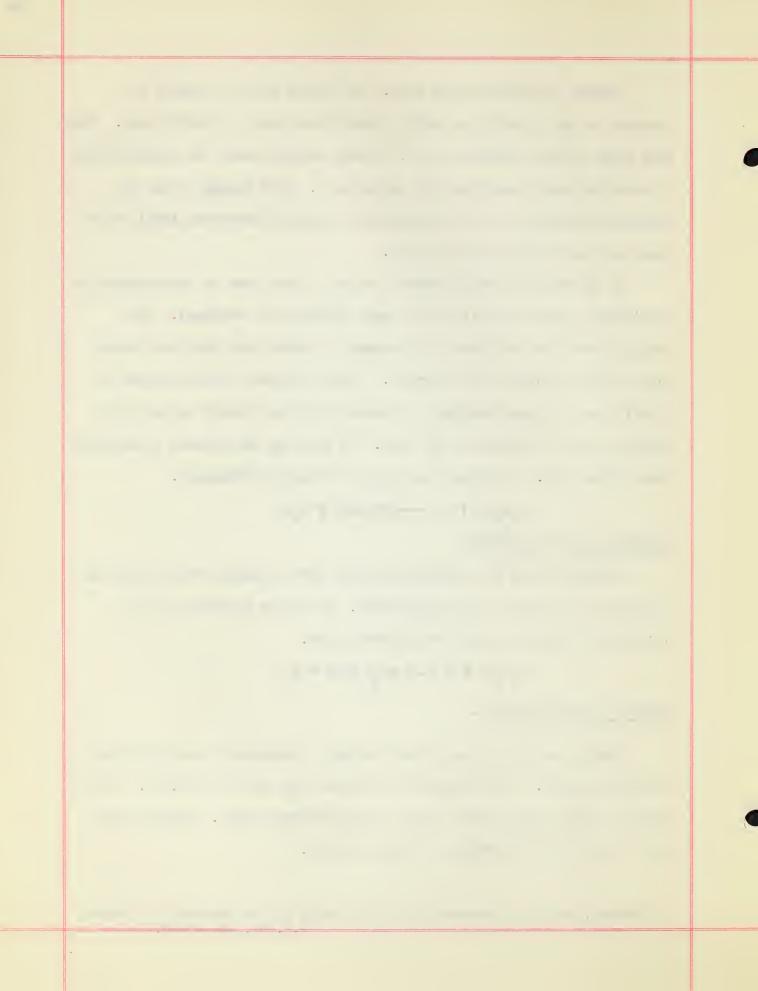
Propionic acid is a colorless liquid with a pungent sour smell, and is miscible in water in all proportions. It can be prepared by the oxidation of propyl alcohol with chromic acid.

$$C_3H_7OH + 2O \longrightarrow C_2H_5COOH + H_2O$$

Butyric acid (C,H,COOH):-

Butyric acid is a sour liquid having a disagreeable odor like that of rancid butter. It is miscible with water and boils at 162.5 °C. It is the acid which gives rancid butter its disagreeable odor. Butyric acid can be made by the oxidation of butyl alcohol.

<sup>5 -</sup> Remsen, Ira - An Introduction to the Study of the Compounds of Carbon P.P. 57, 144 & 146.



## Esters

When an acid reacts with a base, water and a salt are formed.

$$HC1 + NaOH \longrightarrow H_2O + NaCl$$

Although alcohols are not ionized in solution, they contain the hydroxyl radical and are acted upon by acids forming water and an "ester".

"An ester is an organic compound formed when an alcohol reacts with an acid".

The equation as given above resembles one of neutralization. The methyl radical takes the place of the hydrogen of the acid forming methyl chloride and the displaced hydrogen atom combines with the hydroxyl group of the alcohol forming water. This reaction is reversible and concentrated sulphuric acid must be added to remove the water. The sweet smelling constituents of plants are often esters and many substitutes for natural flower and fruit essences are now being produced synthetically.

Many halogen derivatives of the hydrocarbons can be made by the reaction between an alcohol and a halogen acid, for example -

$$\begin{array}{c} \text{CH}_3\text{OH} + \text{HBr} \longrightarrow \text{CH}_3\text{Br} + \text{H}_2\text{O} \\ \\ \text{C}_2\text{H}_5\text{OH} + \text{HCl} \longrightarrow \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O} \\ \\ \text{CH}_3\text{OH} + \text{HCl} \longrightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O} \end{array}$$

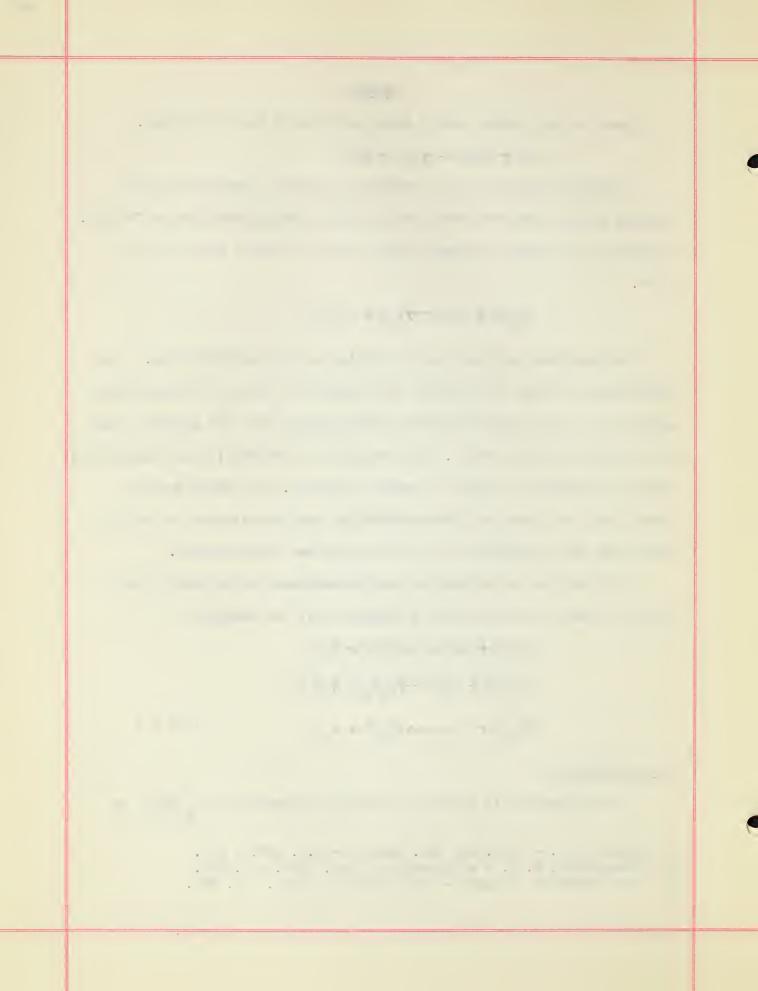
# Nitro-glycerine:-

Nitro-glycerine is an ester formed when glycerine  $(C_3H_5(OH)_3)$  is

<sup>2 -</sup> Dinsmore, E. - Chem. for Sec. Schools - P.P. 337, & 338.

<sup>4 -</sup> Chamberlain, J. S. - A Text-book of Org. Chem. - P. 101.

<sup>20 -</sup> Gray, Sandifora & Hanna - Fundamentals of Chem. - P. 508.



acted upon by nitric acid, thus,

$$c_3H_5(OH)_3 + 3 HNO_3 \rightarrow c_3H_5(NO_3)_3 + 3 H_2O$$

In practice the glycerine is added to a mixture of concentrated sulphuric acid and nitric acid. The sulphuric acid acts as a dehydrating agent and removes the water.

## Fats and oils:-

Fats and oils are esters of glycerine with organic acids called fatty acids. Three of the most important of these acids are oleic acid, palmitic acid, and stearic acid. When an ester is boiled with water or with water and an alkali, it is decomposed into the alcohol and the acid from which it is derived. The alkali present converts the acid into the corresponding salt so that the final products of the reaction are the alcohol and the salt of the acid.

The following equations show the action involved in the hydrolysis of fats.

C<sub>17</sub> H<sub>35</sub> COOH is stearic acid.

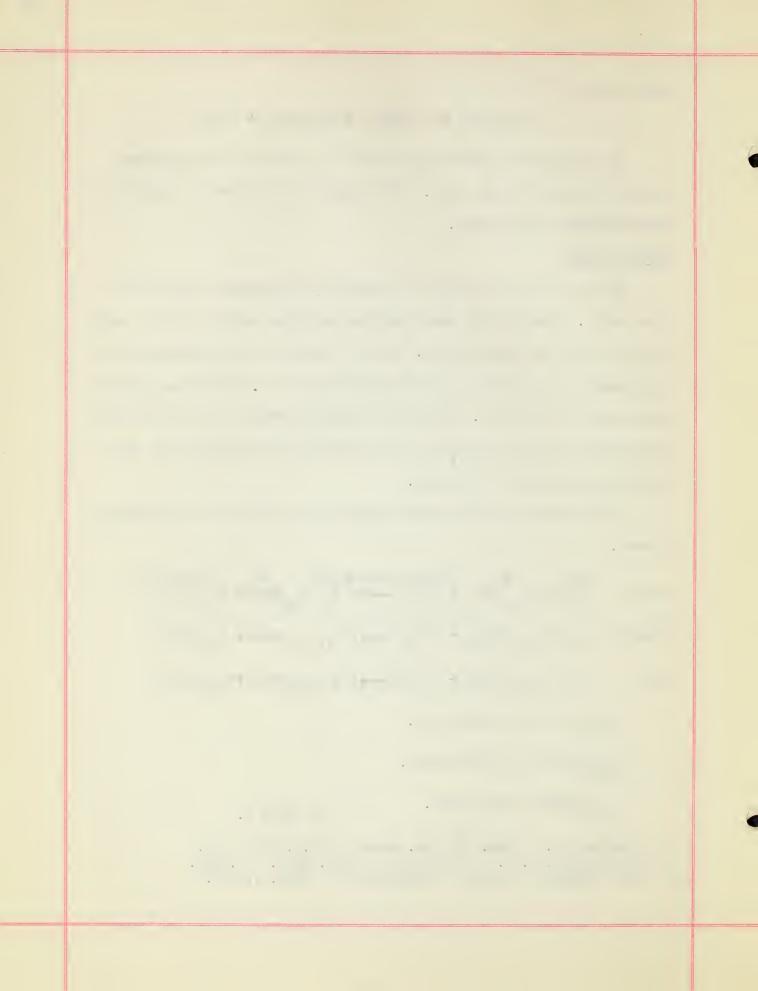
C H COOH is palmitic acid.

C H COOH is oleic acid.

2, 20, & 4.

<sup>2 -</sup> Dinsmore, E. - Chem. for Sec. Schools - P.P. 537 & 338.

<sup>4 -</sup> Chemberlain, J. S. - A Text-book of Org. Chem. - P. 101. 20 - Gray, Sandifur & Hanna - Fundamentals of Chem. P. 508.



When an alkali is present such as sodium hydroxide, the acid formed by hydrolysis is converted into the corresponding salt, thus

Stearic acid Sodium stearate or soap 
$$C_{17}H_{35}COOH + NaOH \longrightarrow H_2O + C_{17}H_{35}COONa$$

Soap is made by boiling fats in a solution of sodium hydroxide. The fats usually contain a mixture of stearin  $(C_3H_5(C_1H_35C00)_3)$ , palmitin  $(C_3H_5(C_1H_35C00)_3)$ , and olein  $(C_3H_5(C_1H_35C00)_3)$ . The boiling of the fats causes them to hydrolize to the acids from which they are derived, the acids being subsequently neutralized by the sodium hydroxide. The equations for the reaction are as follows:-

Stearin Stearic acid Glycerine 
$$C_3H_5(C_{17}H_{35}C00)_3 + 3 H_20 \longrightarrow 3 C_{17}H_{35}C00H + C_3H_5(OH)_3$$
Stearic acid Sodium stearate or soap.  $C_{17}H_{35}C00H + 3 NaOH \longrightarrow 3 H_2O + 3 C_{17}H_{35}C00Na$ 

The above equations may be combined into one equation as follows:-

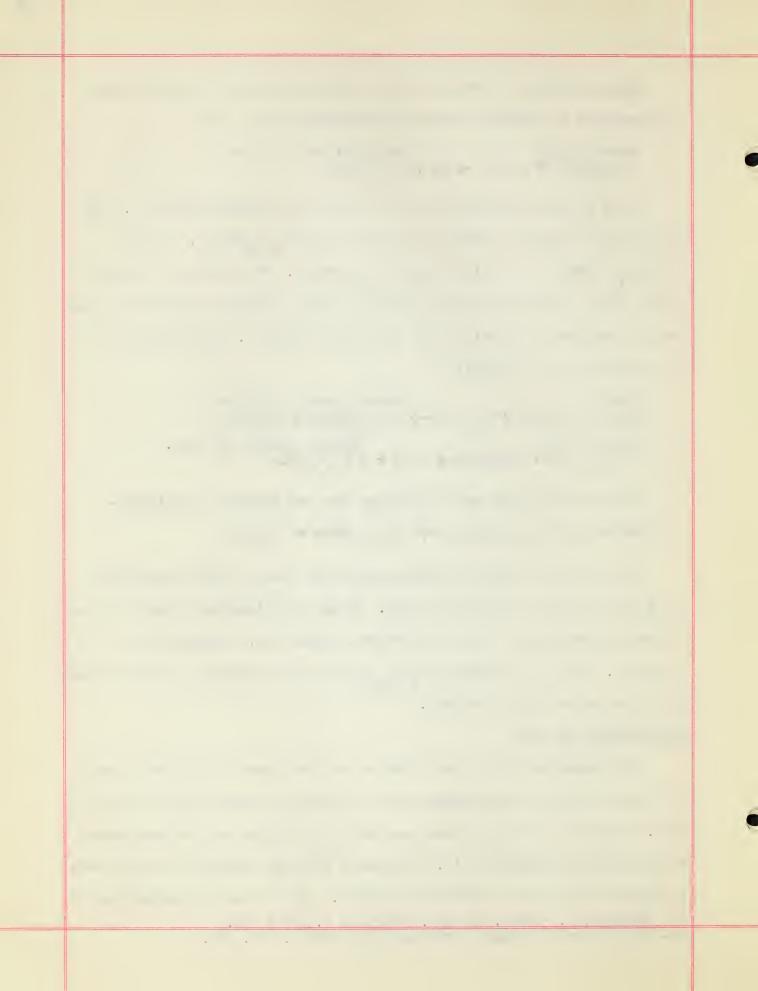
3 NaOH + 
$$_{55}^{\text{H}}$$
 ( $_{17}^{\text{H}}$  25 C00) 3  $\longrightarrow$  3  $_{17}^{\text{H}}$  3 C00Na +  $_{35}^{\text{H}}$  (OH) 3

Palmitin and stearin are white solids and are the chief constituents of hard fats such as tallow and suet. Olein is an important constituent of certain vegetable oils such as olive oil, peanut oil, cotton-seed oil, and palm oil. Lard is a softer fat than tallow or suet because it contains more 2 & 20 olein than either tallow or suet.

#### HYDROGENATION OF OILS

The demand for solid fats suitable for foods and for high grade soaps is responsible for the development of a process for changing oils into solid fats. These fats are often much more valuable for food and the manufacture of soap than the original oils. A molecule of olein contains six less atoms of hydrogen than does a molecule of stearin. If six atoms of hydrogen could 2 - Dinsmore, E. - Chem. for Sec. Schools - P. 337 & 338.

20- Gray, Sandifur & Hanna - Fundamentals of Chem. - P. 508.

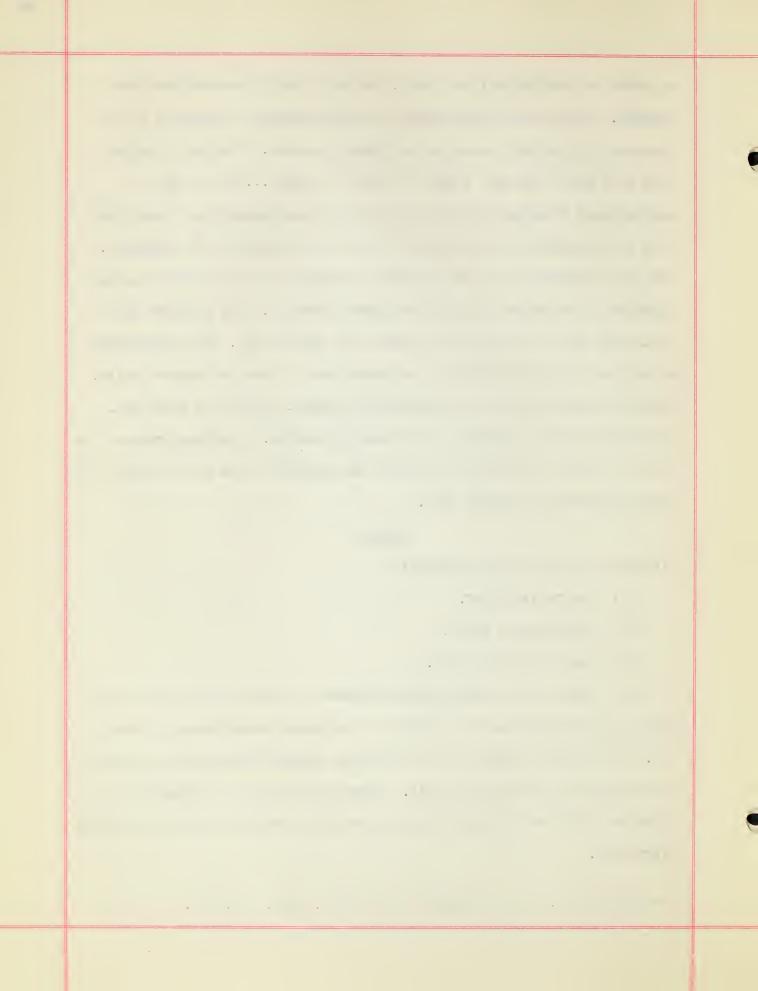


be added to each molecule of olein, the olein could be converted into stearin. This can be accomplished by mixing hydrogen with olein in the presence of a suitable catalyst and under pressure. "Various catalysts have been used, the most import of which is nickel...The oil to be hydrogenated is mixed with the catalyst and then pumped into a tall iron tank or hydrogenator from which all the air is displaced with hydrogen. The oil is agitated with the catalyst by means of a circulating pump and hydrogen is introduced into the oil under pressure. The pressure used varies but may be as high as 25 pounds per square inch. The temperature is held at 175-190°C during the hydrogenation by means of heating coils. When the hydrogenation has proceeded far enough, the oil is drawn off, separated from the catalyst, and allowed to harden." By this process fish oils lose their disagreeable odor and are converted into fats suitable for cooking purposes or making soap.

#### OILS

Oils may be classified as follows:-

- (1) The "fatty oils".
- (2) The "mineral oils".
- (3) The "essential oils".
- (1) Fatty oils include such substances as tallow, lard, olive oil, and cotton seed oil and are extracted from animal carcasses, muts, seeds, etc. They are not capable of distillation without decomposition, and for this reason are called fixed oils. These oils consist of compounds of glycerine with stearic acid oleic acid or other fatty acids and are called glycerides.
- 7 Williams, R. J. An Introduction to Org. Chem. P. 148.



- (2) The "mineral" or "hydrocarbon" oils are obtained from petroleum wells and consist as their name implies almost entirely of hydrocarbons.

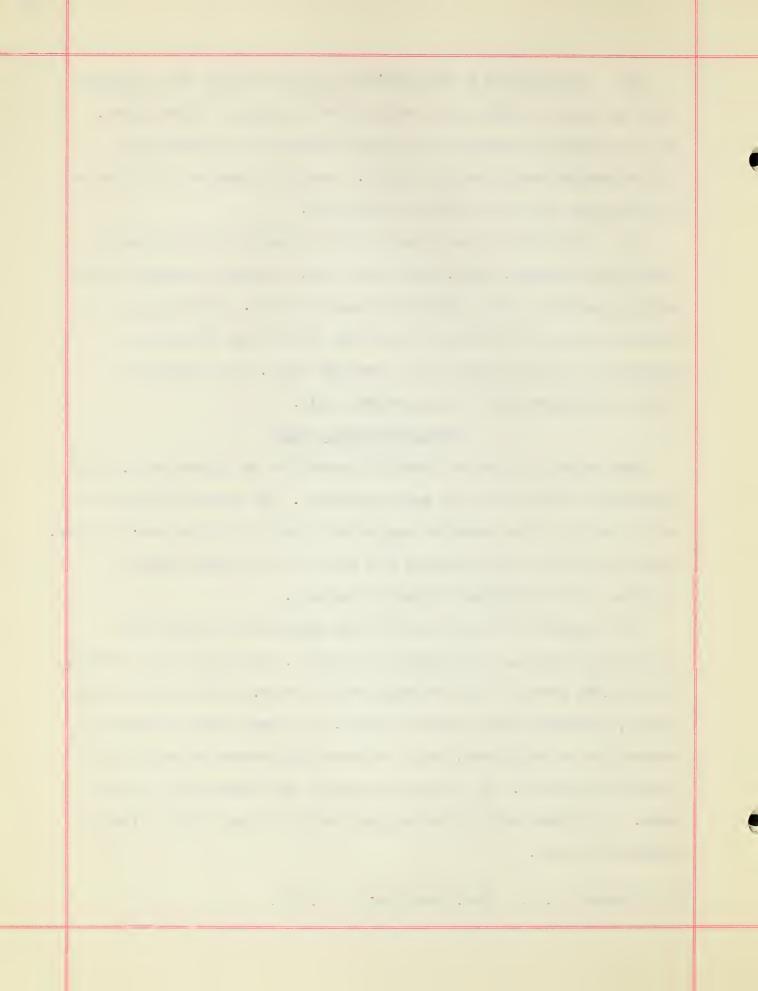
  They are capable of distillation without decomposition and undergo no chemical change when boiled with alkali. They are, therefore, of no use to the soap maker since they cannot be saponified.
- extraction of flowers, twigs, roots, bark, etc., and are obtainable in much smaller quantities than the other two classes of oils. They cannot be converted into soaps but being volatile and some of them possessing a pleasant odor, they are much used in scenting soaps. The aldehydes of higher alcohols are found in many volatile oils.

# THE MANUFACTURE OF SCAP

Soap making is a chemical reaction carried out on a large scale. The reagents are fats and oils and sodium hydroxide. The chemical change that takes place when these materials are boiled together is called saponification. During saponification the fats and oils react with the sodium hydroxide resulting in the formation of glycerine and soap.

The prepared fats and oils and sodium hydroxide are spouted out through pipes into huge three-story-high kettles. Each one of these kettles holds 300,000 pounds of soap or nearly ten car loads. In the bottom of the kettles, perforated steam pipes are coiled. The steam escapes through the perforations to supply heat, and at the same time, churns and boils the ingredients together. It is in these caldrons that saponification takes place. It is here that the fats and soda unite with each other to form glycerine and soap.

10 - Kingzett, C. T. - Chem. Encyclopedia - P. 663.



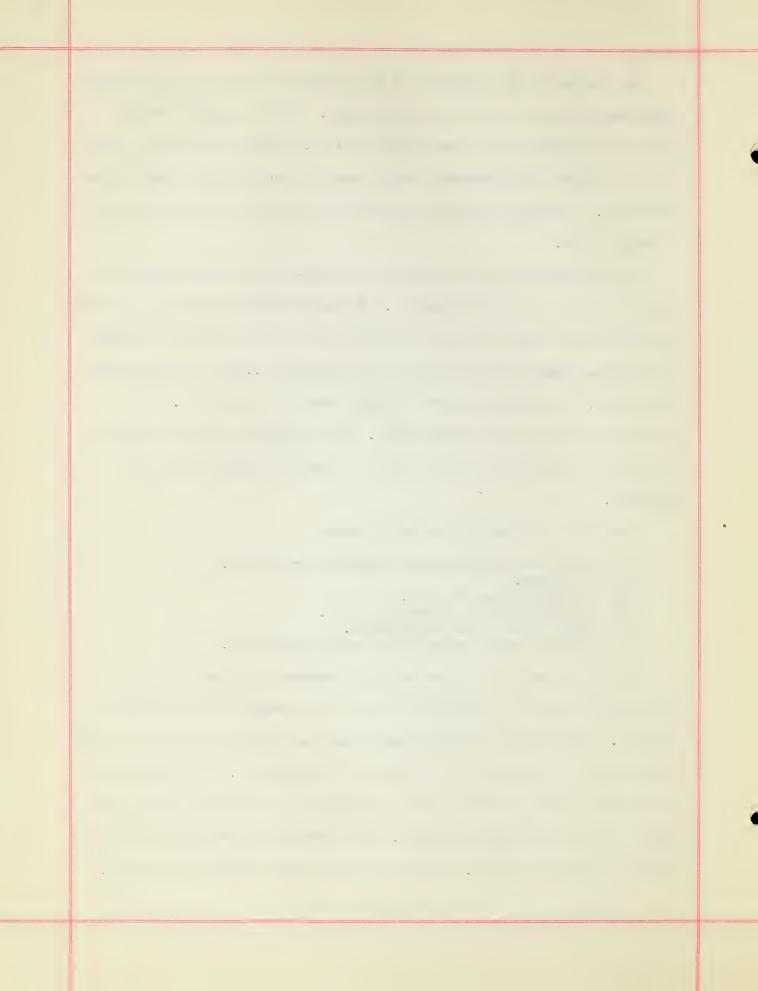
At the top of the caldrons the soap maker stirs the ingredients with a long wooden paddle to test its consistency. When the saponification looks about complete, he throws a small bottle, attached to a chain, down into the caldron and withdraws a small amount of soap which is sent to the laboratory. A careful analysis is made to be sure that the proper change has taken place.

When saponification is complete, the soap-maker proceeds with the next step which is called "graining". He shovels several tons of salt into the kettle which cause the soap to settle out on top of a watery solution of glycerine, unused sodium hydroxide and impurities. When the separation is complete, the watery solution is pumped away to be purified. The glycerine is recovered by distillation. It is distilled again and again and then it is bleached to produce what is known as "chemically pure" glycerine.

Some uses of glycerine are as follows:-

- (1) Anti-freeze solution for automobile radiators.
- (2) Cosmetics.
- (3) A preservative for food.
- (4) Sculptors use it in modeling clay.
- (5) Artists use it in their paints.
- (6) Printers depend upon it for their smooth inks.

The thick soap left in the kettle is washed with water to free it from the last traces of impurities, and is then pumped to the crutching machines. The crutching machines are large mixing machines in which rotary blades churn the soap until it is smooth in consistency. From the crutching machine the soap, which is now a creamy mass, is released into great oblong iron boxes mounted on wheels. These boxes have removable sides and ends and are called frames. Each frame holds about 1000 pounds of soap.

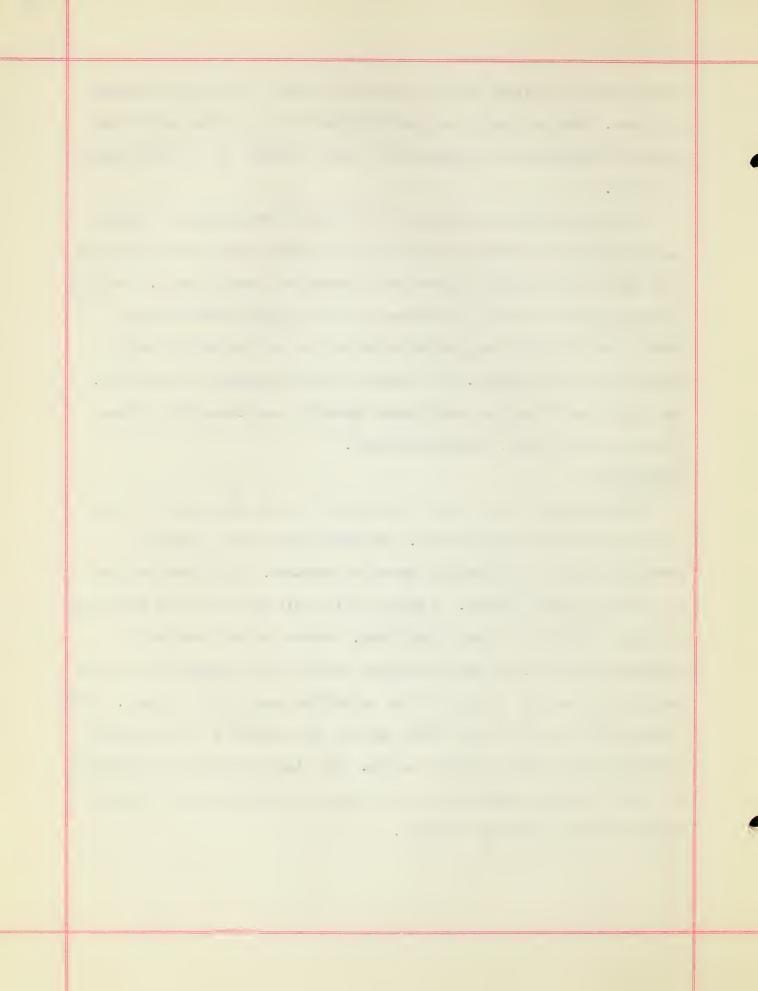


Here the soap is allowed to age and solidify before it is cut and stamped into bars. When the ageing has been completed, the sides and ends of the frame are removed and the gigantic bar is left standing on the truck ready to be cut.

The great blocks of soap are cut by being forced through a slabbing machine which is a framework holding equally spaced piano wires which slice each block into horizontal layers the thickness of a cake of soap. From the slabbing machine the soap is transported to the cutting machine which divides the slabs into long sticks which are cut into cakes by a cross motion of the same machine. All cutting is done by means of piano wires. The rough bars of soap are next pushed through a long tunnel drier after which they are stamped, wrapped and boxed.

# Flake soap:-

The making of flake soap is the same as that of cake soap up to the point where it leaves the kettles. The semi-liquid soap is piped to crutchers where it is thoroughly mixed and smoothed. It is then run from the crutchers into a trough. A great chilled roll dips into this trough and picks up a thin film of semi-liquid soap. Before the roll has made a complete revolution, the soap has become chilled, and a long knife in close contact with the roll scrapes off the solidified soap in thin ribbons. These ribbons fall on a wire screen which carries them through a drying chamber, discharging them into a conveyer system. The flakes are swept by compressed air into pipes that convey them to the boxing room where they are boxed by machine and made ready for shipment.



# Soap granules:-

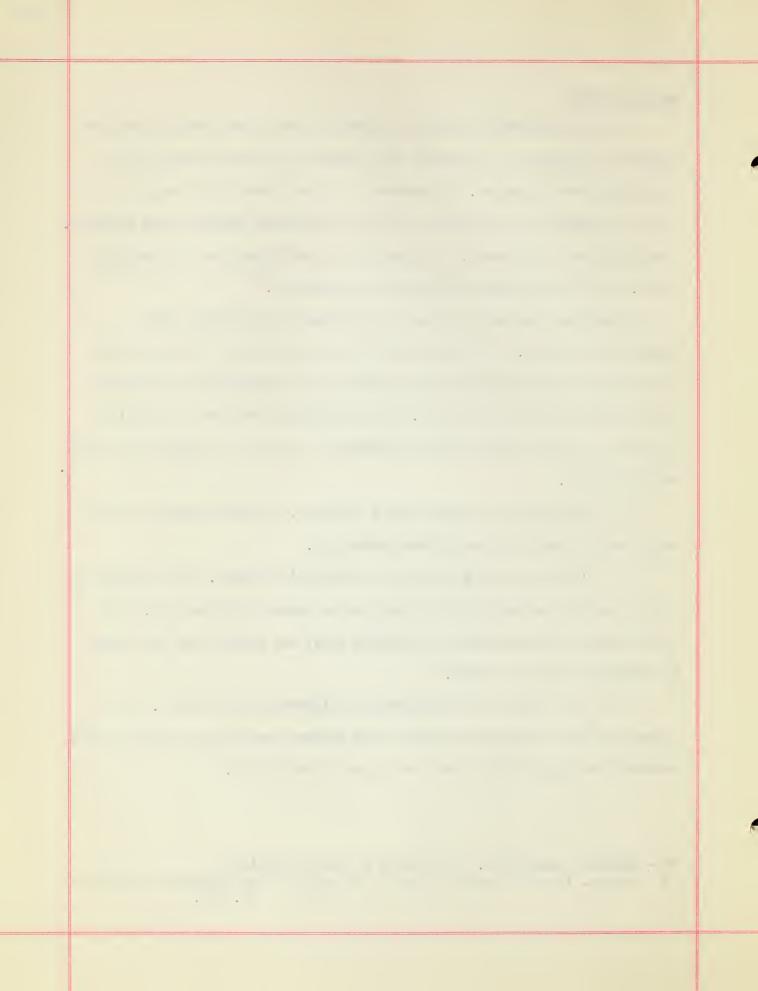
In the manufacture of soap granules the semi-liquid soap leaving the crutchers is pumped to the top of tall towers and sprayed through small nozzles by steam pressure. It emerges as a fine, sudsy mist, and, as it falls the length of the towers, it forms into minute bubble shaped granules. From the base of the tower, the product is carried away to be thoroughly dried. It is then packed and weighed by machinery.

Glycerine has many uses, and is a valuable by-product of the manufacture of soap. Yet its recovery as pure glycerine is so difficult that chemists have tried to separate fats into fatty acids and glycerine before making soap from the fats. Several methods are used to hydrolyze the fats into free fatty acids and glycerine of which the following are the most important.

- (1) By heating with water under pressure, a small amount of lime or zinc oxide being added to aid the hydrolysis.
- (2) "By heating with water and Twitchell's reagent. This reagent is made by heating commercial oleic acid and an aromatic hydrocarbon, like naphthalene, with concentrated sulphuric acid, and washing out the excess of sulphuric acid with water."
- (3) "By heating with concentrated sulphuric acid to 120°C. This method not only hydrolyzes the fats into glycerol and fatty acids, but also converts the liquid oleic acid into a solid fatty acid".

<sup>23 -</sup> Proctor & Gamble Co. - The Story of Soap (Pamphlet)

<sup>5 -</sup> Remsen, Ira - An Introduction to the Study of the Compounds of Carbon P. 165.



# Ethers

The ethers may be considered as derived from alcohols by replacing the hydrogen of the hydroxyl group by an organic group such as  ${\rm CH_3}$  or  ${\rm C_2H_5}$  etc. Thus,

Ethyl alcohol Di-ethyl ether or di-ethyl oxide

"These radicals in ethers may be alike or different. The ethers are as a rule colorless, very volatile, pleasant smelling liquids. They are chemically rather inert and are good solvents for many substances. Di-ethyl ether is used as an anaesthetic and is sometimes called 'sulphuric ether' because it is made from ethyl alcohol by treatment with sulphuric acid."

The only member of the series that is of importance is di-ethyl ether or ordinary ether.

When methyl alcohol is treated with sodium, a compound having the formula CH3-0-Na ( sodium methylate ) is formed.

$$2 \text{ CH}_3 \text{OH} + 2 \text{ Na} \longrightarrow 2 \text{ CH}_3 \text{-O-Na} + \text{H}_2$$

Likewise when ethyl alcohol is treated with sodium a compound having the formula  ${\rm C_2H_5}{\text{-}0{\text{-}}{\rm Ha}}$  (sodium ethylate) is formed.

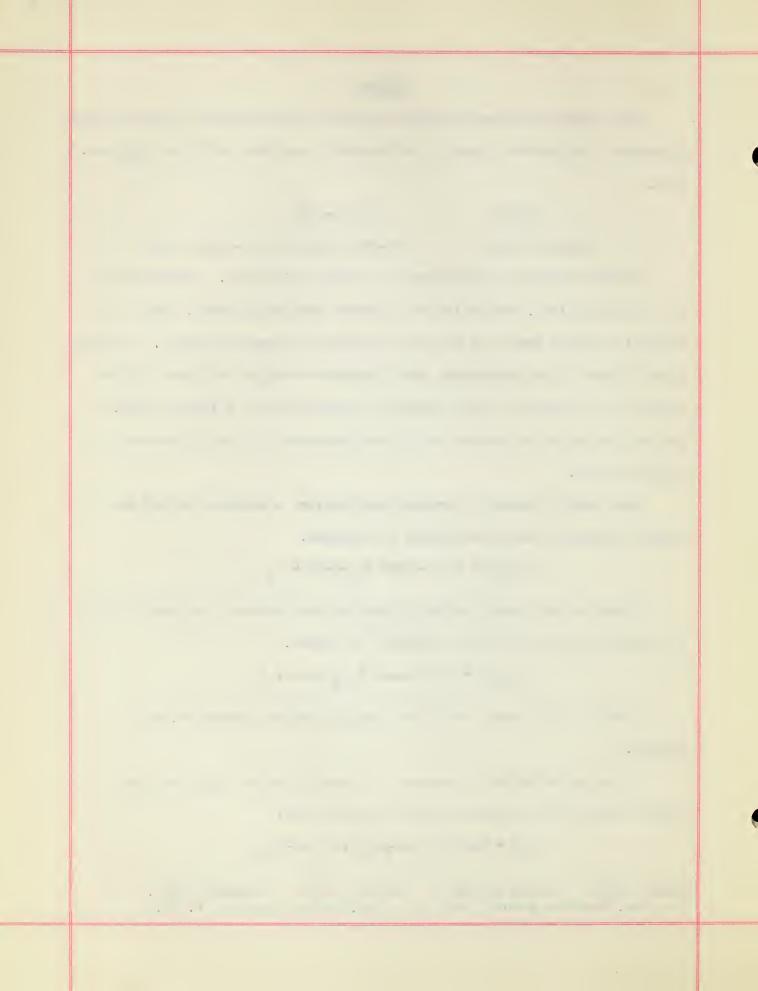
$$2 C_2H_5OH + 2 Na \longrightarrow 2 C_2H_5-O-Na + H_2$$

Alcohols like water react with metallic sodium, potassium, and calcium.

If sodium methylate is treated with methyl iodide (CH3I) and the mixture warmed, the following reaction takes place:-

$$CH_3I + Na-O-CH_3 \longrightarrow Nal + CH_3-O-CH_3$$

Methyl iodide sodium methylate sodium iodide di-methyl ether. 3 - Chem. Warefare School, Book II - Chem. Warfare Agents - P. 79.



Likewise, if sodium ethylate is warmed with ethyl iodide ( $C_2H_5I$ ) the following reaction takes place:-

Ethyl iodide + sodium ethylate - sodium iodide + di-ethyl ether.

Ether is made on a large scale by heating sulphuric acid and ethyl alcohol in certain proportions and then distilling the mixture. In this process equal molecular parts of ethyl alcohol and sulphuric acid are mixed together and heated to 140°C. More alcohol is then added and ether produced. The reactions which take place are as follows:-

$$\begin{array}{c} C_2H_5OH + \stackrel{H}{\downarrow} SO_4 \longrightarrow \stackrel{C_2H_5}{\longrightarrow} SO_4 + H_2O \\ H \\ Ethyl sulphuric acid. \end{array}$$

With the addition of more alcohol, the ethyl sulphuric acid formed reacts with the excess of alcohol forming ethyl ether and sulphuric acid.

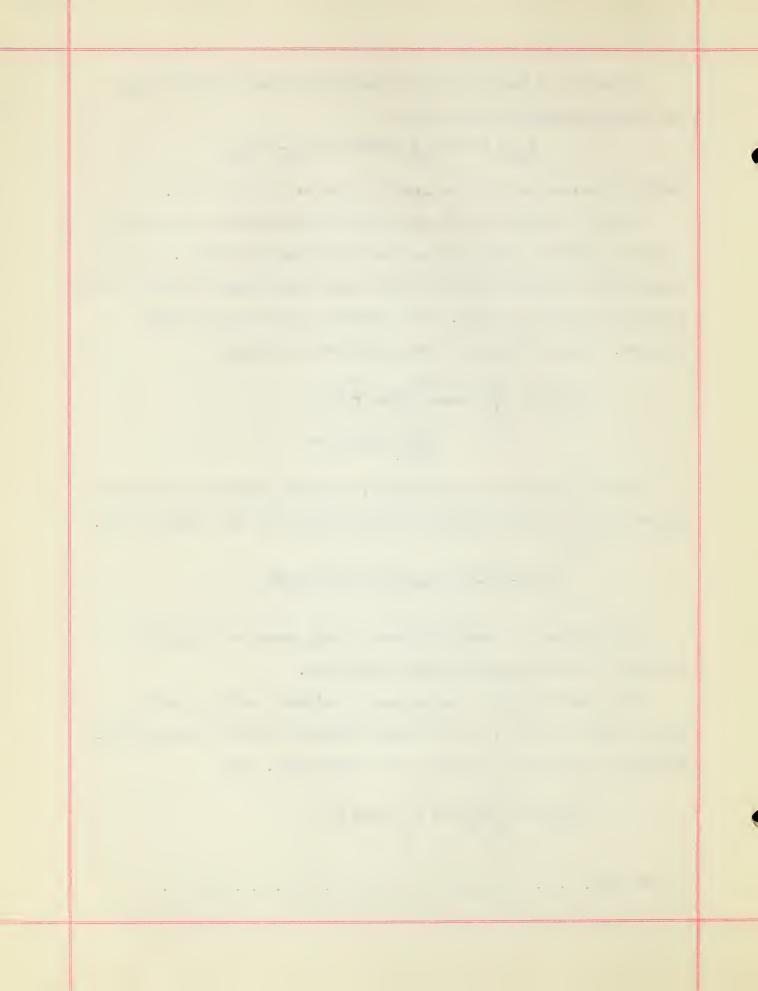
$$c_{2}^{H}$$
  $c_{2}^{H}$   $c_{2$ 

This process is a continuous one, a small amount of sulphuric acid converting a large amount of alcohol into ether.

When double molecular proportions of sulphuric acid are used, the mixture heated to 160°C, and additional sulphuric acid and alcohol added, ethylene is produced and sulphuric acid regenerated. Thus,

$$c_{2}H_{5}OH + \prod_{H} so_{4} \longrightarrow c_{2}H_{5} so_{4} + H_{2}O$$

7 - Williams, R. J. - An Introduction to Org. Chem. P.P. 65 & 77.



With the excess of sulphuric acid the ethyl sulphuric acid yields

4
ethylene and sulphuric acid is regenerated.

### Ketones

### Acetone: -

"This substance has long been known as a product of the distillation of acetates. It is present in considerable quantities in the products of the distillation of wood, and is separated from the mixture after the removal of acetic acid".

Acetone can be obtained by the distillation of calcium or barium acetate. When calcium acetate is distilled, a liquid having the formula C<sub>3</sub> 60 passes over and calcium carbonate is left behind. The reaction takes place in accordance with the following equation:-

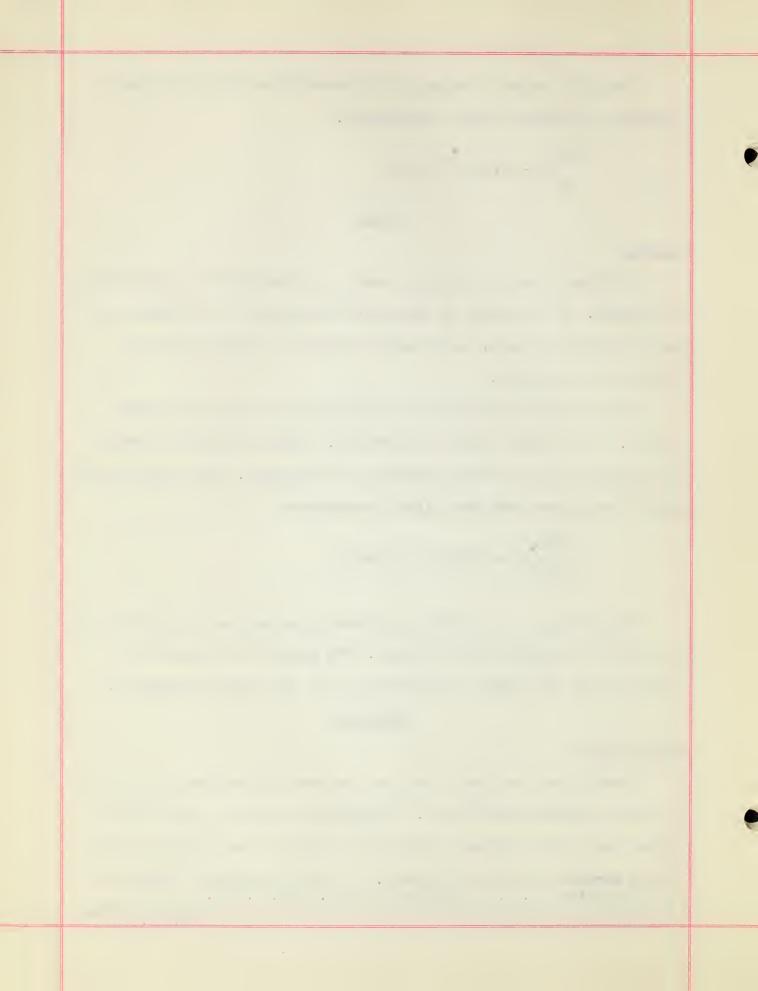
$$CH_3COO$$
 $Ca \longrightarrow CaCO_3 + CH_3 - CO - CH_3$ 
 $CH_3COO$ 

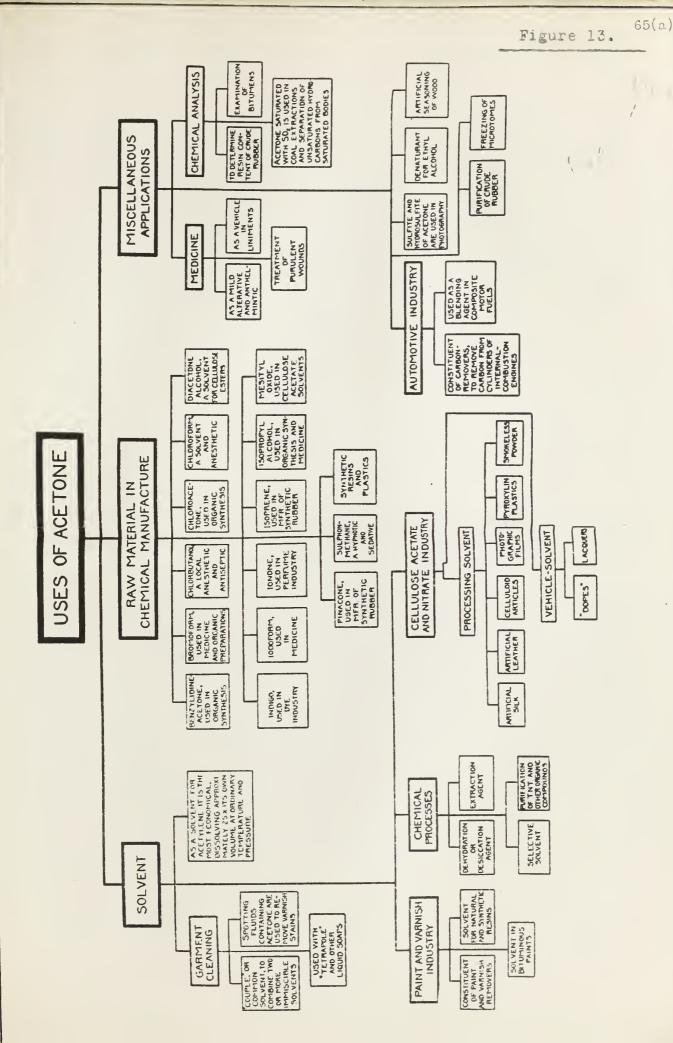
(CH3-CO-CH3) is the formula representing acetone and is the best known of a class of compounds called ketones. The ketones all contain the carbonyl group (CO) which is characteristic of this class of compounds.

#### COSMETICS

# Rouge sticks:-

Rouge sticks are almost invariably colored with carmine, either with or without treatment with alkali. Since the user desires a color effect rather than a greasy effect, lipsticks are generally made fairly hard and with a maximum percentage of pigment. The carmine content should not 4 - Chamberlain, J. S. - A Text-book of Org. Chem. P. 160. 5 - Remsen, Ira - An Introduction to the Study of the Compounds, of Carbon -







exceed 20%, but the majority are made with less. If a bright color is desired it can be obtained by the addition of zinc oxide.

The general method of manufacture consists of melting and straining the fats and oils and milling the pigment with the warmed mass. The liquified product is run into moulds where it solidifies. A typical formula for lipsticks is given below:-

Carmine 50 grams

Ammonia A sufficient quantity

White wax 450 grams

Peach kernel oil 500 C.C.

Benzyl Propionate 1 C.C.

## MANICURE PREPARATIONS

# Softening cream: -

The healthy condition of the cuticle can be maintained by the nightly application of a softening cream. This also prevents the nails from becoming brittle or ribbed. Such creams almost invariably contain soap and preference is given to the soft potash varieties. A typical formula for softening cream is as follows:-

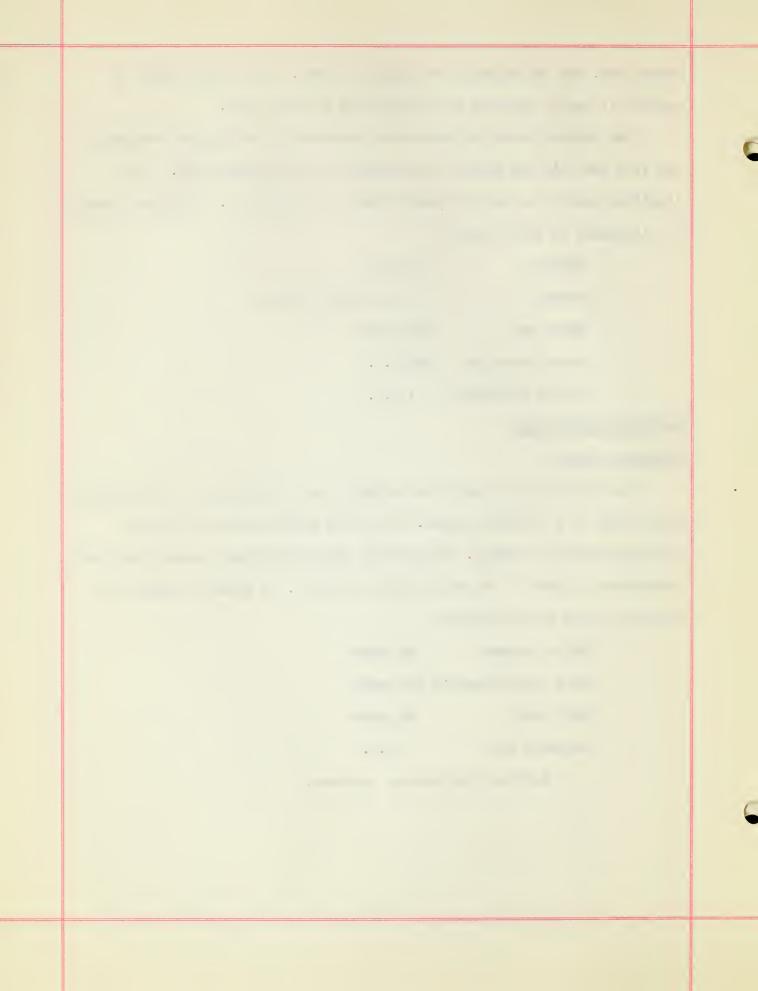
White beeswax 10 grams

Soft paraffin-white 950 grams

Soft soap 40 grams

Lavender oil 5 C.C.

Melt the ingredients together.



# Cuticle remover:-

The most effective type of solution for removing cuticle is made with caustic potash and glycerine as follows:-

Potassium hydroxide 20 grams

Glycerine 200 grams

Water 800 grams

Bergamot oil 1 C.C.

# Nail bleaches:-

Nail bleaches are used to remove discolorations, ink stains, etc.

A typical formula for a nail bleach is as follows:-

Oxalic Acid 15 grams

Phenylacetic acid 1 gram

Water 1000 C.C.

# Nail polish:-

A liquid nail polish may be prepared as follows:-

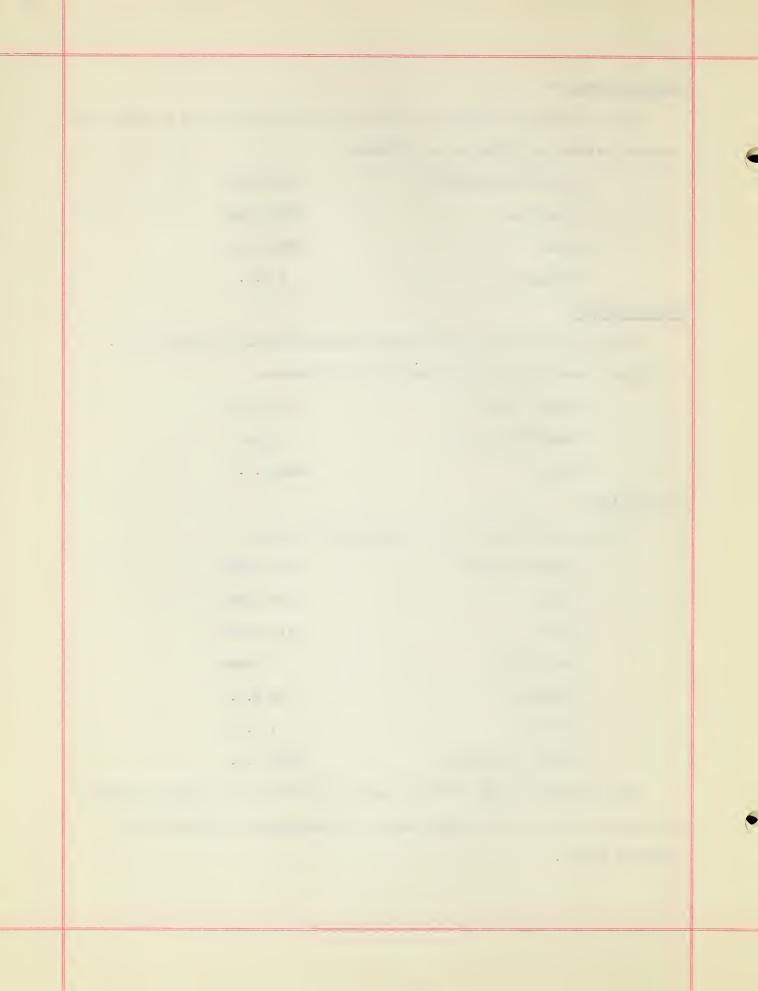
Stannic oxide300 gramsTalcum300 gramsKaolin100 gramsTragacanth2 grams

Glycerine 50 C.C.

Citral 1 C.C.

Water to produce 1000 C.C.

Nail polishes in the form of blocks or sticks can be made by massing the powders given in the formula above with mucilage of tragacanth and allowing to dry.



### Nail enamel:-

An enamel can be made as follows:-

Cellulose acetate 25 grams

Tetrachlorethane 550 C.C.

Acetone 450 C.C.

## COLD CREAM

A typical formula for cold cream is as follows:-

Almond oil 550 C.C.

White wax 150 grams

Borax 10 grams

Water 290 C.C.

Rose otto 5 C.C.

## FACE POWDER

A formula for face powder is as follows:-

Rice starch 600 grams

Maize starch 200 grams

Talcum 100 grams

Zinc stearate 50 grams

Zinc oxide 50 grams

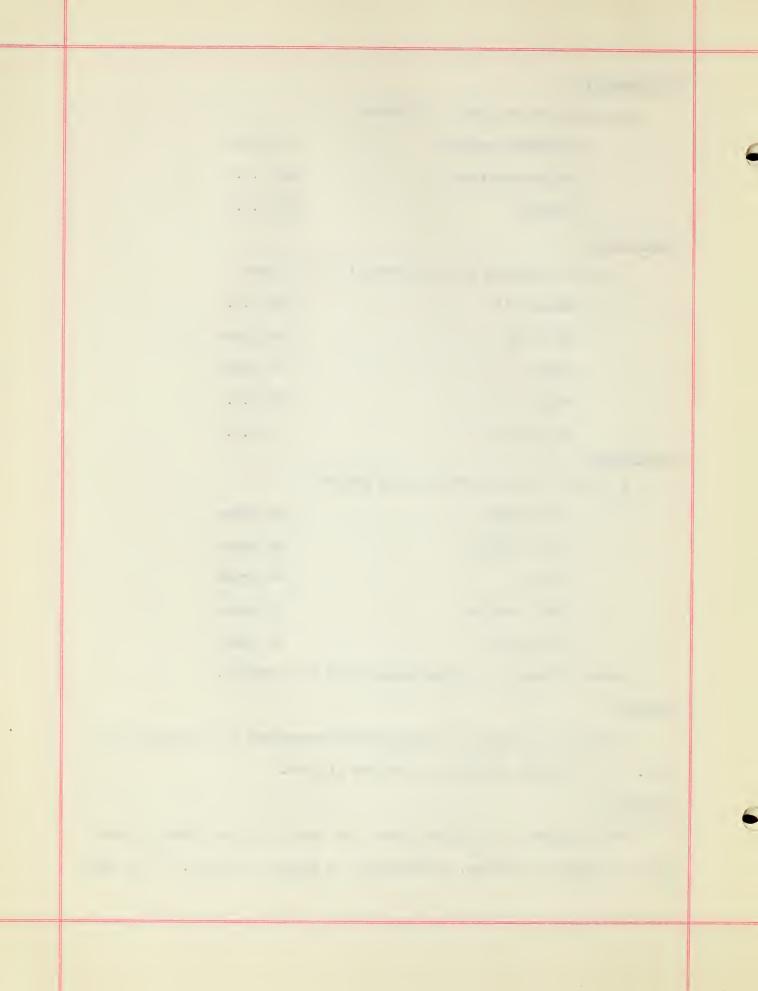
Source of some of the substances used in cosmetics.

## Carmine:-

Carmine is prepared by precipitating decoctions of cochineal with alum. It is readily soluble in alkaline liquids.

#### Cochineal:-

The cochineal is an insect about the size of a tick, found in the warmer climates of America, particularly in Oaxaca in Mexico. It is found



on several species of cactus. The insects are gathered and put in a pot where they are confined for some time and then killed by the application of heat. These insects thus killed form a mass called cochineal.

### Beeswax:-

Beeswax is produced by bees from the sugar of their food. It is somewhat yellow, tough and solid, of complex composition and can be bleached by chlorine or hydrogen peroxide.

# Rose otto:-

This is obtained by distilling the fresh flowers. The distilled oil is pale yellow and has a S.G. of 0.850 at 30°C. Otto of roses is frequently adulterated with geranium oil, and is chiefly used in perfumery.

### Almond oil:-

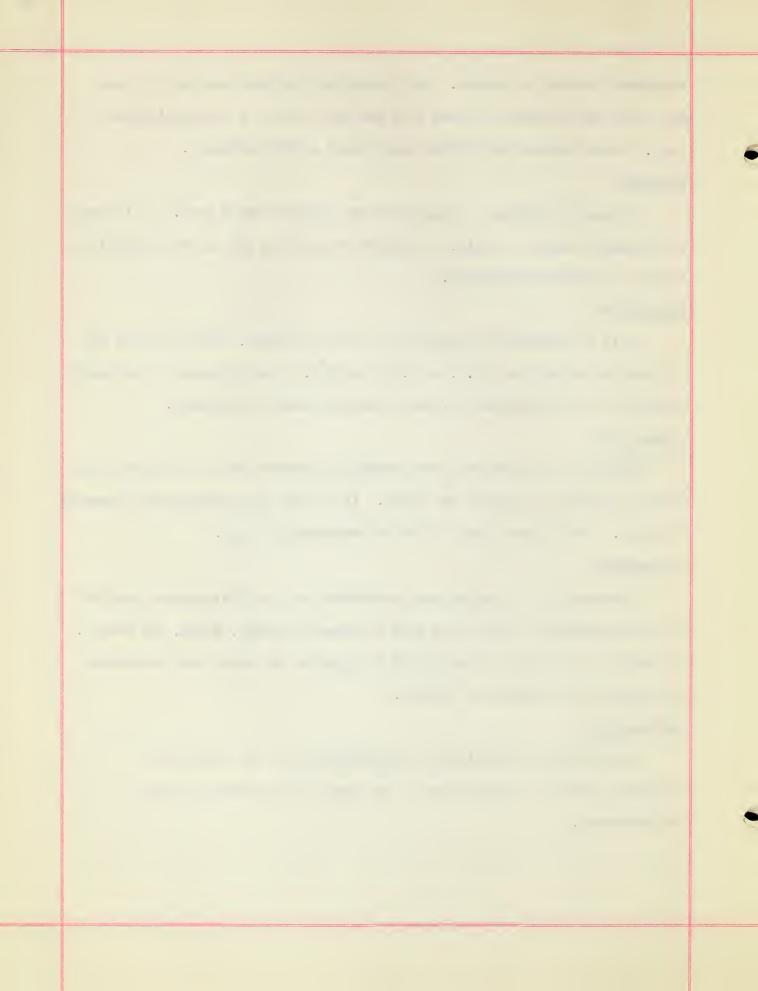
Almond oil is extracted from almonds by pressure and is a yellowish oil which is soluble in alcohol and ether. It is used for scenting and flavoring purposes. Its fragrant odor is due to benzaldehyde  $^{7}_{76}$ 0.

# Tragacanth:-

Tragacanth is a mucilaginous exudation from the "Astragalus Cummifer" and "Microcephalus" trees which grow in Armenia, Turkey, Syria, and Persia. It swells up in water and half of it is soluble; the other part consisting of starch also dissolves on boiling.

#### Lavender oil:-

Lavender oil is obtained by distillation from the flowers of "Lavendula Vera", a plant native of the lower alps bordering on the Mediterranean.



# Bergamot oil:-

The bergamot is a species of citron whose fruit has a fine taste and smell. The fruit is shaped like a pear. Its oil is in high esteem as a perfume and is extracted from the yellow rind of the fruit.

Citral:-

Citral is an essential oil extracted from the rind of lemons.

Peach kernel oil:-

This is the oil extracted from the kernel of peachstones.

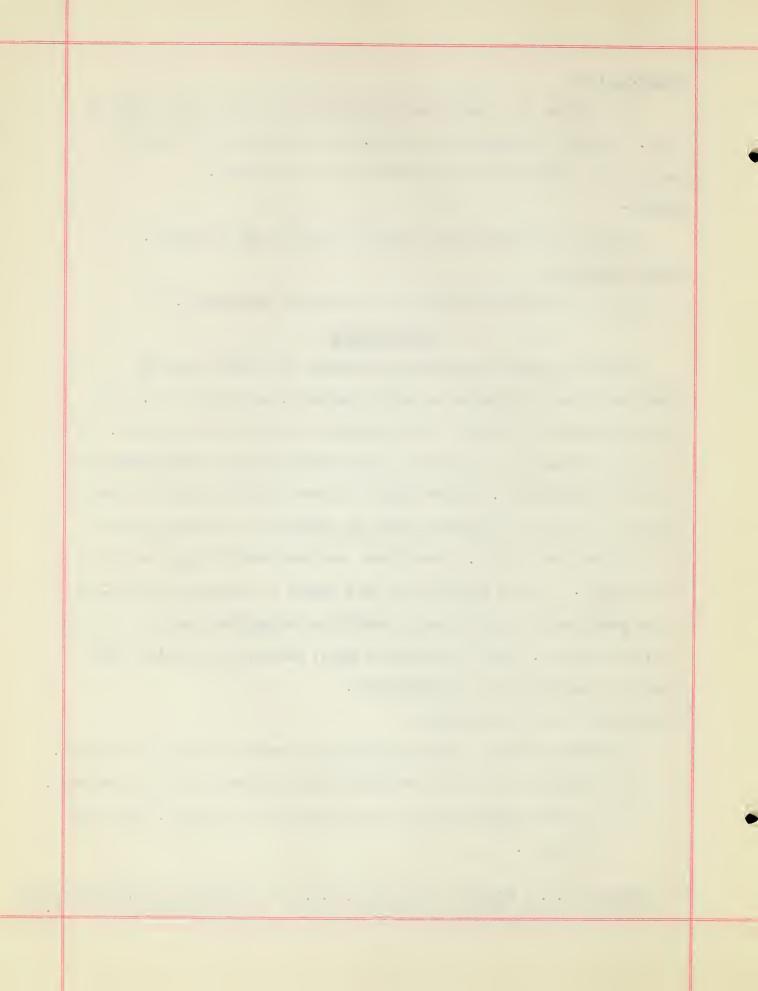
### CARBOHYDRATES

There is a group of exceedingly important and widely occurring substances which are composed of carbon, hydrogen, and oxygen only. The ratio of hydrogen to oxygen in these compounds is the same as in water. It is for this reason that this class of compounds have been called hydrates of carbon or carbohydrates. However there are some substances which, as far as molecular formulas are concerned, might be considered as carbohydrates but are not classified as such. Among these are formaldehyde ( $\mathrm{CH}_2\mathrm{O}$ ) and lactic acid ( $\mathrm{C}_3\mathrm{H}_6\mathrm{O}_3$ ). A rigid definition of what should be included in this class is not possible, and yet the term is useful in designating a class of closely related substances. Such substances as sugar, starch, and cellulose come under the classification of carbohydrates.

Carbohydrates may be classified as:-

- (1) Monosaccharides those containing six carbon atoms to the molecule.
- (2) Disaccharides those containing twelve carbon atoms to the molecule.
- (3) Colloidal polysaccharides such as cellulose  $(C_6H_{10}O_5)_x$ . and starch  $(C_6H_{10}O_5)_x$ .

<sup>24 -</sup> Poucher, W.A. - Perfumes & Cosmetics, P.P. 377, 578,381,382,383,385,388 & 427 5 - Remsen, Ira - An Introduction to the Study of the Compounds of Carbon - P.212



### Sugar

Among the most important sugars are "sucrose" or cane sugar (beet sugar also), "levulose" or fruit sugar, "maltose" or malt sugar, "lactose" or milk sugar, and dextrose or grape sugar. The following table gives the names and formulas of these sugars:-

Levulose C6H12O6

Dextrose C6H12O6

Maltose C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

Lactose C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

Sucrose C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

By observing the above table it can be seen that some of the compounds have the same empirical formula, yet their properties are not identical.

Such compounds are known as isomers and their difference in properties is due to different arrangement of the atoms in the molecule.

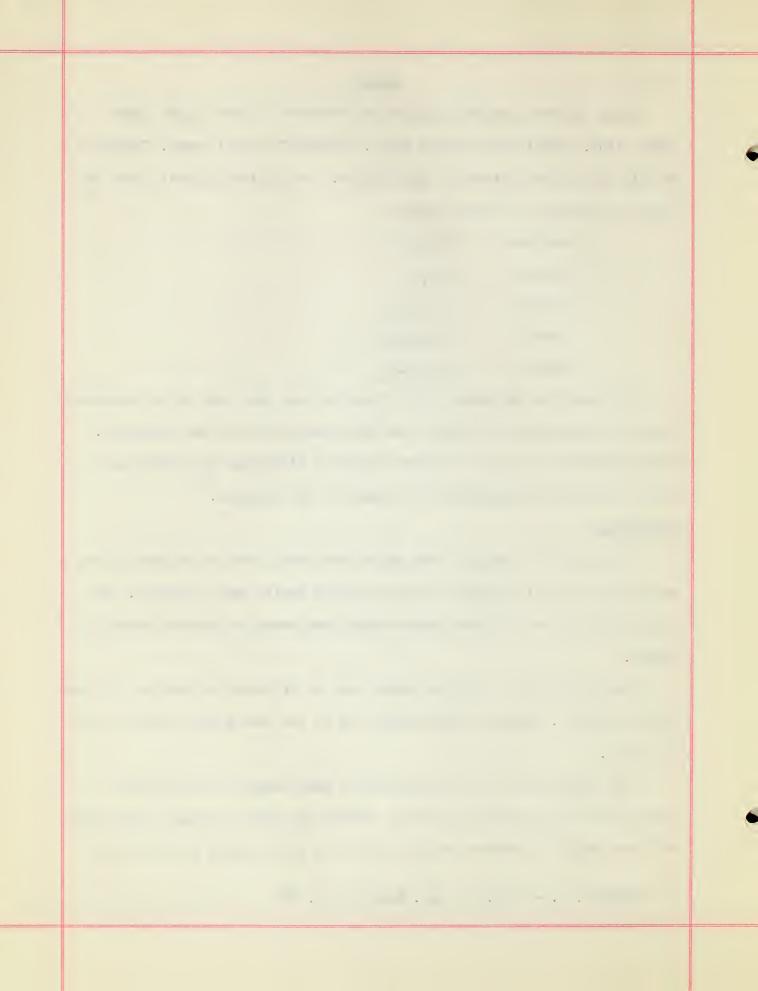
## CANE SUGAR:-

Cane sugar is produced from sugar cane which grows in stalks of from one to two inches in diameter and from six to twelve feet in height. The yield of sugar from the sugar cane varies from seven to fifteen percent by weight.

The planting of a field of sugar cane is effected by planting cuttings from the stalks. Numerous shoots grow out of the buds around each joint of the stalk.

The operations in the manufacture of cane sugar are as follows:
Upon arrival at the mill the cane is crushed and ground through a series of revolving rolls to extract the juice which is then treated with lime and

2 - Dinsmore, E. - Chem. for Sec. Schools - P. 348



heated to remove impurities. The "bagasse" (the remaining cane fibre) is used in the boiler room as fuel. After being limed the juice is pumped through heaters, allowed to settle in tanks, and passed to evaporators for concentration to a thick syrup. The syrup is then boiled at a low temperature under a vacuum until the water content has been sufficiently reduced to bring about crystallization of the sugar. The greater part of the molasses is then expelled by means of centrifugals. The product remaining in the centrifugals is raw sugar which is a light brown color on account of the molasses not being entirely removed by the centrifugals. Upon leaving the centrifugals the raw sugar is ready to be bagged for shipment to the refinery.

In Louisiana the "bagasse" is used for the manufacture of celotex, which is a good substitute for lumber for some building purposes. It is also used in the making of fibre boxes for shipping freight. In this way it becomes more valuable than when used for fuel.

In some mills a good deal of molasses is used for fuel by burning it in the furnaces with bagasse or fuel oil to make steam. As there is a great deal of potassium in the ash thus formed, it is valuable as a fertilizer. Some molasses is also made into fuel alcohol.

Refining of sugar:-

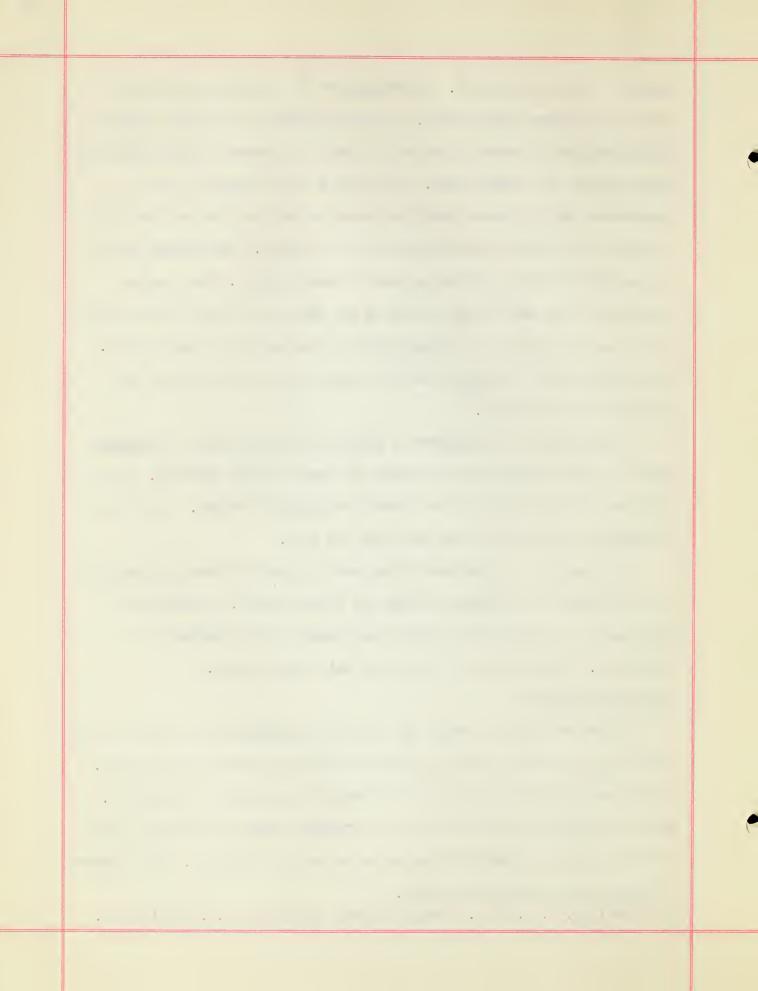
At the refinery the sugar is carried on conveyers up to the top floor where it is mixed with syrup and then sent through centrifugal machines.

The purpose of this is to wash out as ruch of the molasses as possible.

When the sugar comes out it is known as "washed" sugar and contains about 99% pure sugar and about 1% of molasses and other impurities. This process

25 - Harriman, W. A. & Co. - Sugar, A Basic Industry - P.P. 13, 16 & 17.

is known as the affination process.



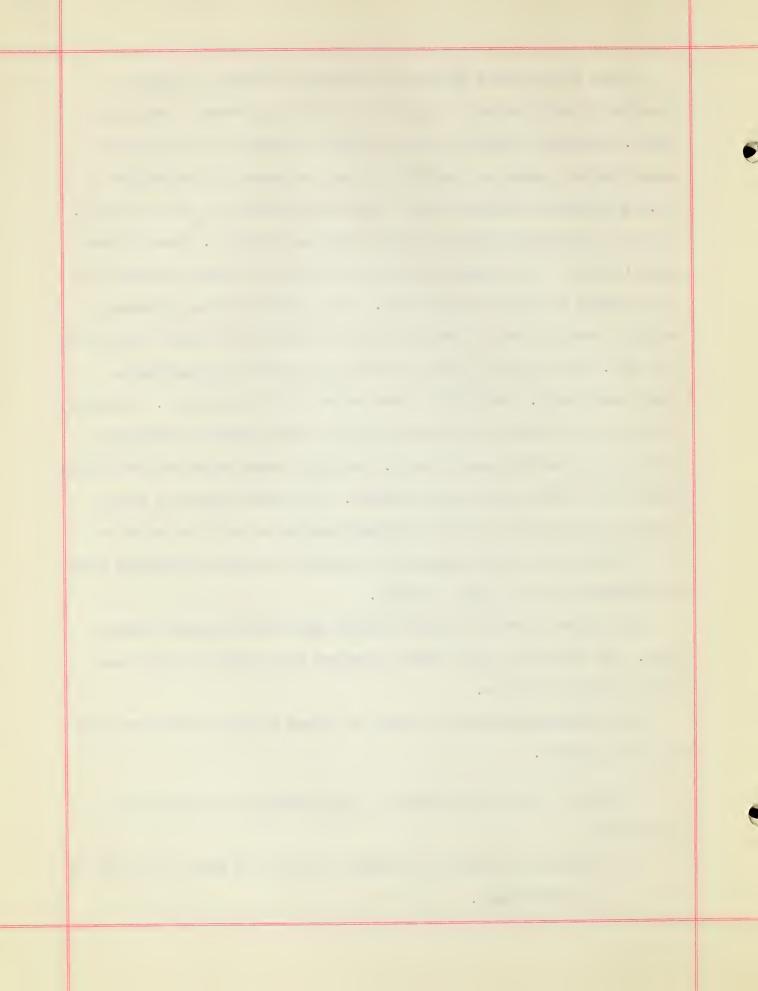
After it has passed through the affination process, the sugar is dissolved in syrup and this is purified by filtering through a bone char filter. Bone char looks like small pieces of charcoal and is made from bones which are broken up into little pieces and heated in the absence of air. When bones are heated in this manner they blacken but do not burn up. Bone char has wonderful power of taking color out of sugar. When the dark syrup is made to pass through the bone char filters, it comes out clear and white, having lost all its dark color. These filters are big cylinders, sometimes twenty or thirty feet tall and about one half as wide, filled with bone char. The dark syrup goes in at the top and comes out underneath almost water white. The syrup is then boiled in big vacuum pans. After the water has been removed, the sugar is put into centrifugals to separate the liquid syrup from the sugar crystals. The sugar comes out of the centrifugal machines as a white crystalline substance. It is next dried in a slowly revolving drier after which the different sizes of crystals are sorted out by a bolting machine which consists of a series of sieves of different sized mesh through which the sugar is passed.

Cube sugar is made by mixing a little syrup with the white refined sugar. The thick paste thus formed is pressed into moulds just the size of the cubes by a machine.

The refining completed, the sugar is placed in bags or boxes and made ready for shipment.

A summary of the steps involved in the refining of raw sugar are given below:-

(1) Affination process - raw sugar is mixed with syrup and purged in centrifugals.



- (2) Sugar is dissolved in syrup.
- (3) Syrup solution thus formed (2) is filtered through bone char filters.
- (4) White syrup is boiled down to white sugar.
- (5) Crystals are separated from syrup in centrifugals.
- (6) Crystals separated in (5) are dried.

26

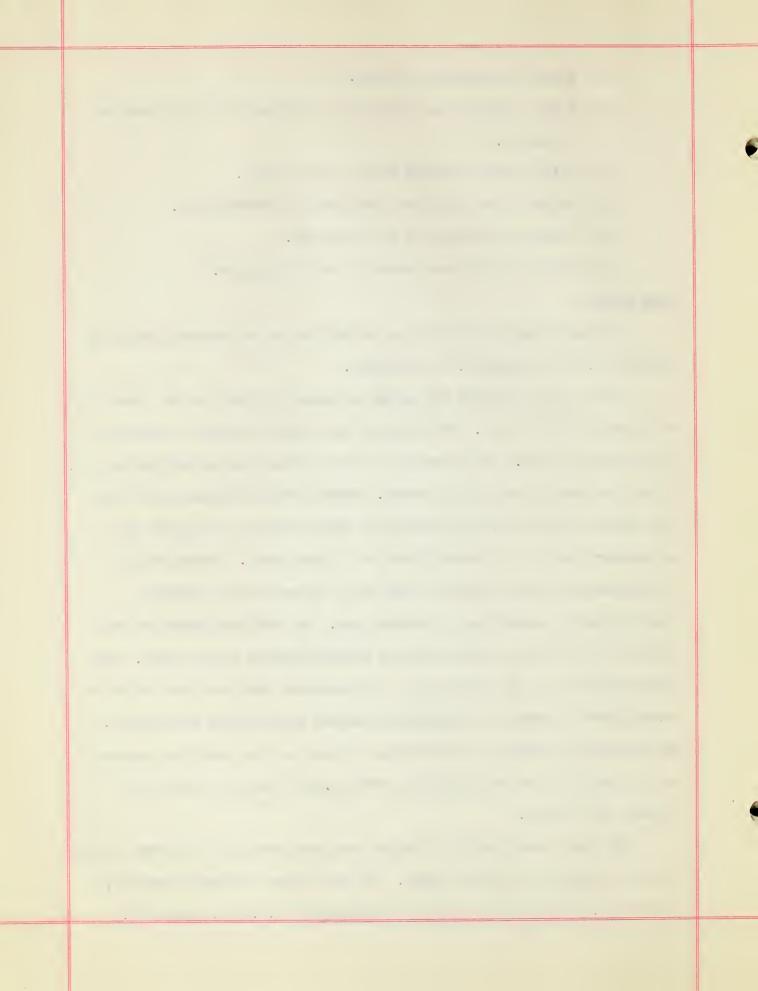
(7) Dried crystals are sorted in bolting machine.

## BEET SUGAR:-

The beet sugar industry in the United States is located chiefly in California, Utah, Colorado, and Michigan.

After being harvested the beets are washed, sliced and the juice is extracted with hot water. To coagulate the impurities, lime is added and the solution heated. The solution is then treated with carbon dioxide gas, allowed to settle, and then filtered. After further treatment with lime and carbon dioxide gas, the solution is again filtered and passed into evaporators where it is concentrated to a thick syrup. Treatment with sulphurous acid fumes follows, after which the solution is further concentrated by evaporation in vacuum pans. In this last operation the reduction of the water content causes crystallization of the sugar. The final operation is the separation of the molasses from the sugar which is accomplished by means of centrifugal machines revolving at a high rate. The molasses is expelled by centrifugal force, and the resulting product which remains in the centrifugals, after being washed with water, is refined white sugar.

"The beet sugar industry differs from the cane sugar industry in that the final product is refined sugar. The cane sugar producers generally 26 - Univ. of Hawii - The Story of Kane Sugar - P.P. 103, 106 & 107.



market their product in the raw state and leave the refining to be done by 25 other companies."

#### STARCH:-

Starch is made from Indian corn and the separation of the starch from the corn is largely mechanical. The corn is soaked in warm water containing some carbon dioxide and when soft is passed through a mill in order to break it up. The germ which is at the apex of the kernel and contains most of the oil floats when the mass is mixed with water and can be separated by screening. The watery mass is further ground and passed through sieves which remove the fibrous material and allow the starch suspension to pass through. Starch is obtained as a sediment in quite pure condition when the starch solution is allowed to settle. Starch prepared in this manner is sold under the names of corn starch and laundry starch.

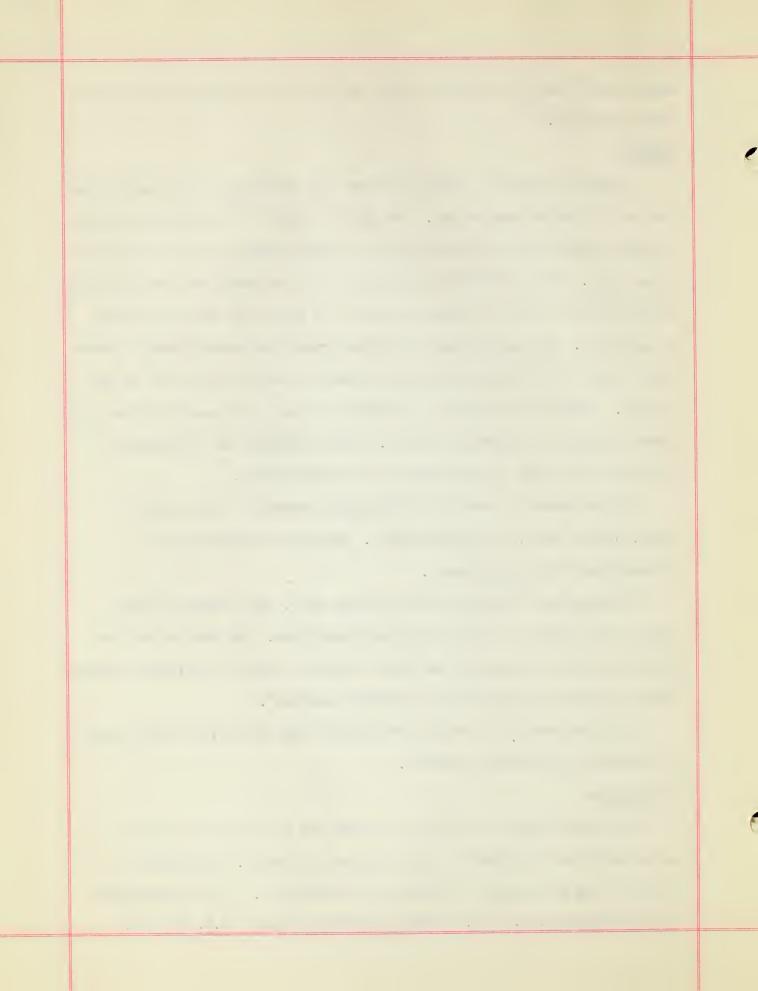
Starch occurs in nearly all plants and composes a large part of maize, barley, oats, rice and potatoes. Chemically starches are carbohydrates (polysaccharides).

Although not soluble in water, starch will, when heated in water, swell up and assume a more or less pasty condition. The heat causes the grains of starch to swell up and burst, forming a kind of emulsion, commonly known in chemical laboratories as "starch solution".

When treated with a cold dilute mineral acid for several days starch is converted into "soluble starch".

#### Corn syrup:-

When corn starch is boiled with water and a little acid such as hydrochloric acid is added, a sugar, glucose is formed. The glucose  $(C_6H_{12}O_6)$  can be obtained in crystals by evaporation. In the manufacture 25 - Harriman, W. A. & Co. - Sugar, A Basic Industry - P.P. 12 & 13.



of corn syrup the evaporation is stopped before crystallization begins and the syrup is sold for making candy and preserving fruits. In this process the hydrochloric acid acts as a catalytic agent in the conversion of starch to glucose and is later neutralized with sodium carbonate forming sodium chloride which remains in the glucose. Sodium chloride is used to season 7 foods and does no harm.

$$^{\text{C}_{6}\text{H}_{10}\text{O}_{5} + \text{H}_{2}\text{O}} \longrightarrow ^{\text{C}_{6}\text{H}_{12}\text{O}_{6}}$$

Starch combines with iodine forming a deep blue compound which serves as a test for starch.

Cellulose occurs as the cell wall of plants. Several special forms of cellulose occur as fibres of various plants such as cotton, flax, and wood. The cellulose contained in these plants have an immense economic value. Cotton fibre is practically pure cellulose..It is extensively used in the manufacture of paper, gun-cotton, nitro-cellulose lacquers, silk substitutes, artificial hair, cellophane, and in the preparation of celluloid films. Pure cellulose is prepared as follows:-

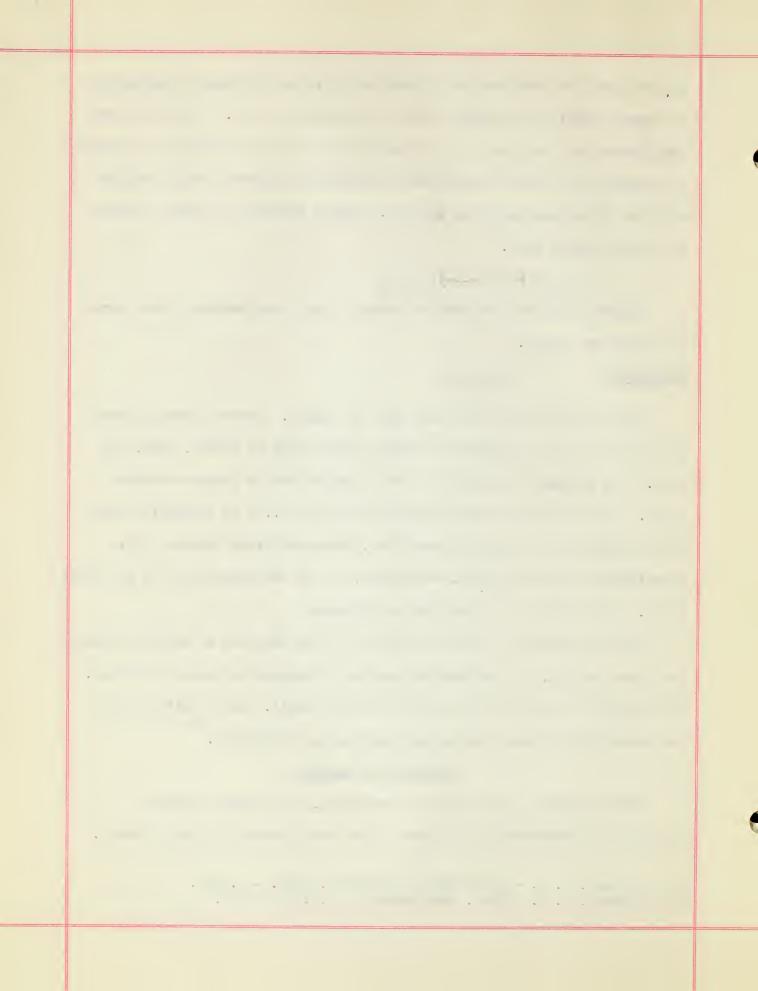
The raw material is boiled with a 1% to 2% solution of sodium hydroxide and after washing, the undissolved portion is exposed to gaseous chlorine.

This product is again boiled with the dilute alkali, thus eliminating all 10 the non-cellulose constituents and yielding pure cellulose.

# ALCOHOL FROM SAWDUST

Wood contains a great deal of cellulose, which under suitable conditions is converted into glucose which when fermented yields alcohol.

7 - Williams, R. J. - An Introduction to Org. Chem. - P. 341. 10 - Kingzett, C. T. - Chem. Encyclopedia - P.P. 159 & 160.



At Los Angeles wood waste and sawdust is subjected to a process of treatment with hydrochloric acid gas under pressure, whereby glucose 80% fermentable is obtained. By this process 65 to 70 gallons of alcohol are yielded per 10 ton of sawdust.

### PAPER

Paper making consists in uniting or felting together any fibrous substances so as to form a continuous sheet. Any substance possessing a sufficient fibrous structure can be utilized. Old rags and other forms of cellulose are useful. The processes that the different forms of cellulose undergo before being made into paper may be divided into four main branches (1) cleaning (2) boiling (3) bleaching (4) beating and reducing to pulp.

(1) Cleaning:-

This is purely a mcchanical process and consists of removing sand and dirt from the raw material.

(2) Boiling:-

The rags are boiled with alkali under pressure in huge revolving cylinders. The proportion of alkali, used depends on the state of the rags, the nature of the substances to be removed, the steam pressure employed, and the duration of the operation.

(3) Bleaching:-

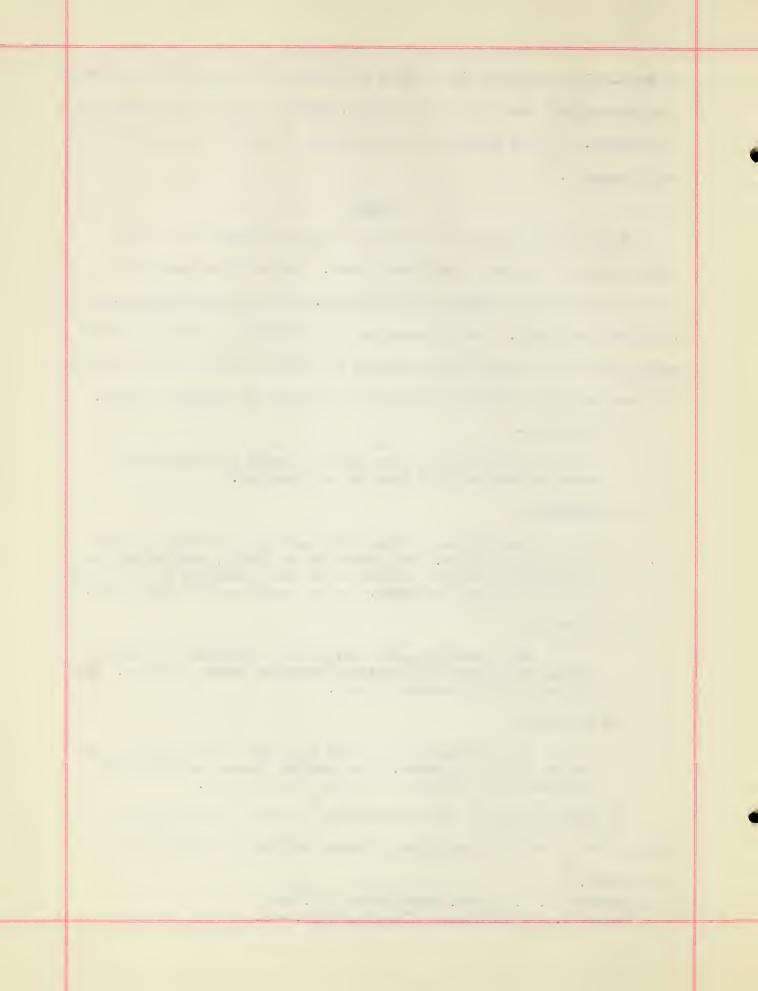
The bleaching agent employed is a solution of calcium hypochlorite, made by dissolving bleaching powder in water. The action is often hastened by heat.

(4) Beating:-

The bleached pulp, before being made into paper must be beaten up into fragments. This beating process completes the disintegration produced by boiling and bleaching.

The paper is made by the deposition of the pulp (finely divided fibers) from a state of suspension in water, followed by rolling and 27 calendering.

10 - Kingzett, C. T. - Chem. Encyclopedia - P. 409 27 - Thorpe, T. - A Dictionary of Applied Chem. - P. 54



#### TEXTILES

#### Cotton:-

Cotton is cultivated in many countries and on account of its cheapness is of great value in the chemical industry. It is obtained from the cotton plant and consists of long white fibres which protect the seeds of the plant. These fibres consist of 90% to 95% cellulose and are in the form of hollow cylinders which twist as they dry. In spinning the twist causes the cotton fibres to cling together, thus making it possible to produce thread of any desired length. The density of cotton is high and its elasticity is low. This causes cotton garments to be heavy and not hold their shape. Being a better conductor of heat than animal fibres, it does not give as good protection from the cold.

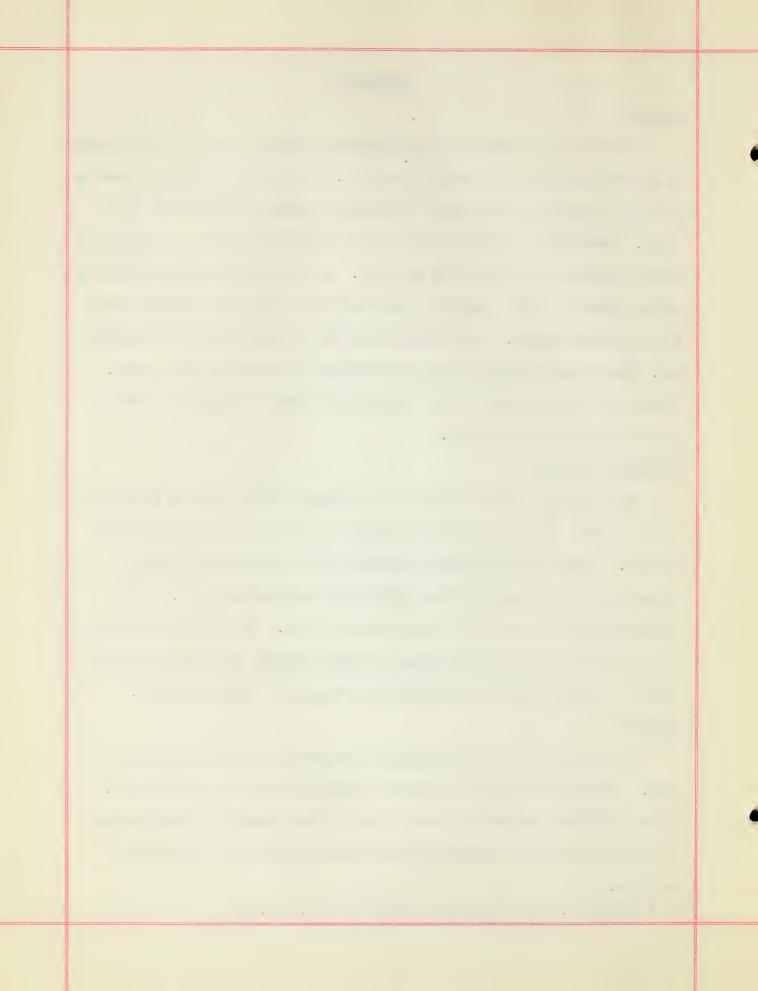
# Mcrcerized cotton:-

When cotton cloths or yarn, in a stretched condition, are immersed in a caustic soda solution of 18-25% strength a silk like lustre is imparted to them. Under this treatment the hollow cotton fibres swell up, by thickening into cylinders without practically any hollow space. This phenomenon was discovered by John Mercer in 1844. The process, now carried on under the name of mercerization, not only produces an exceedingly high lustre on the cotton but also increases its power of absorbing dyes.

#### Linen; -

Linen yarn and cloth are manufactured from the fibres of the flax stem. Linen yarn is stated to usually contain about 25% of impurities. These impurities are removed more or less by the bleaching process which is effected by means of hypochlorites after scouring with an alkaline solution.

27 - Thorpe, T. - A Dictionary of Applied Chem. - P. 401



Linen is cellulose the same as cotton. The difference in properties of the two substances, being due to difference in cell formation. The individual fibres of linen are larger and longer than cotton fibres. Linen has high tensile strength, and is prized for its high luster and dazzling whiteness. It does not hold dyes very well and for this reason it is usually sold as white goods. The better grades of linen are bleached by exposure to the sun, since chemical bleaching robs it of some of its appearance and wearing quality.

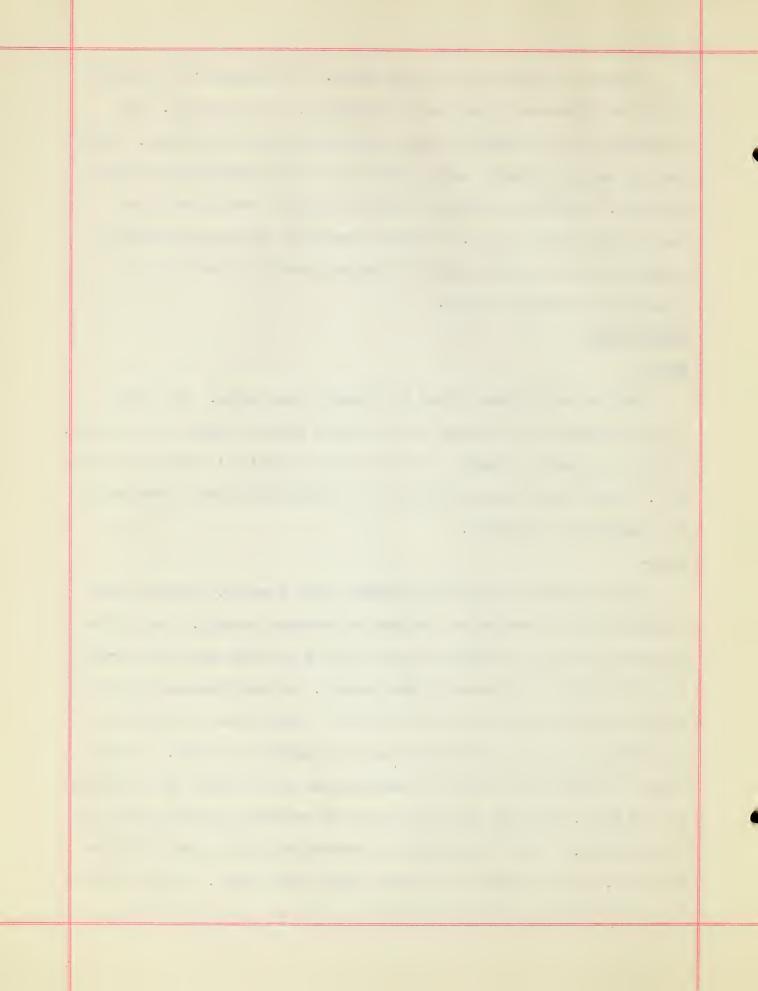
# ANIMAL FIBRES

### Wool:-

Wool is the cleansed fibres from sheep or goat skins. It is of a protein character (all proteins contain carbon hydrogen oxygen and nitrogen). It has high tensile strength, is elastic and hence holds its shape and wears well. Being a poor conductor of heat, it is a desirable fabric for use in the manufacture of garments.

### Silk:-

After reaching maturity the silkworm spins a cocoon, requiring about three days for its completion, in which he envelopes himself. The silk is obtained by heating the cocoon in ovens to kill the pupa, and then by reeling off the silk and spinning it into threads. Although attempts have been made to introduce the silk industry into this country, the cultivation of the silkworm is still confined essentially to Asiatic countries. The silk thread is coated with a kind of a wax which has to be removed in the process of silk dying. This wax like material can be removed by boiling with a hot soap solution. If all this material is removed the silk is called "boiled off silk", and is stronger for the same weight than before. Stannic chloride



is used in weighting silk. After the fibres have been de-gurmed, they are steeped in a solution of that compound and subsequently washed. The term "pure silk" is used in the silk trade for silk which has been weighted just 10 enough to make up for the weight lost in boiling off.

# Artificial silk:-

If a mixture of nitric and sulphuric acid is allowed to react with cellulose, nitric acid esters of cellulose are formed. Collodion is a mixture of nitric acid esters of cellulose, made by nitrating cellulose incompletely. In one method for the manufacture of artificial silk, a thick solution of collodion in a mixture of alcohol and ether is forced by pressure through capillary tubes of very small bore. As the solvent rapidly evaporates, fine fibres of artificial silk are obtained. The artificial silk so made is not explosive, but is very inflammable. To make its use safe the nitrocellulose is denitrated. This is accomplished by treating the nitro-cellulose with ammonium hydrogen sulphide.

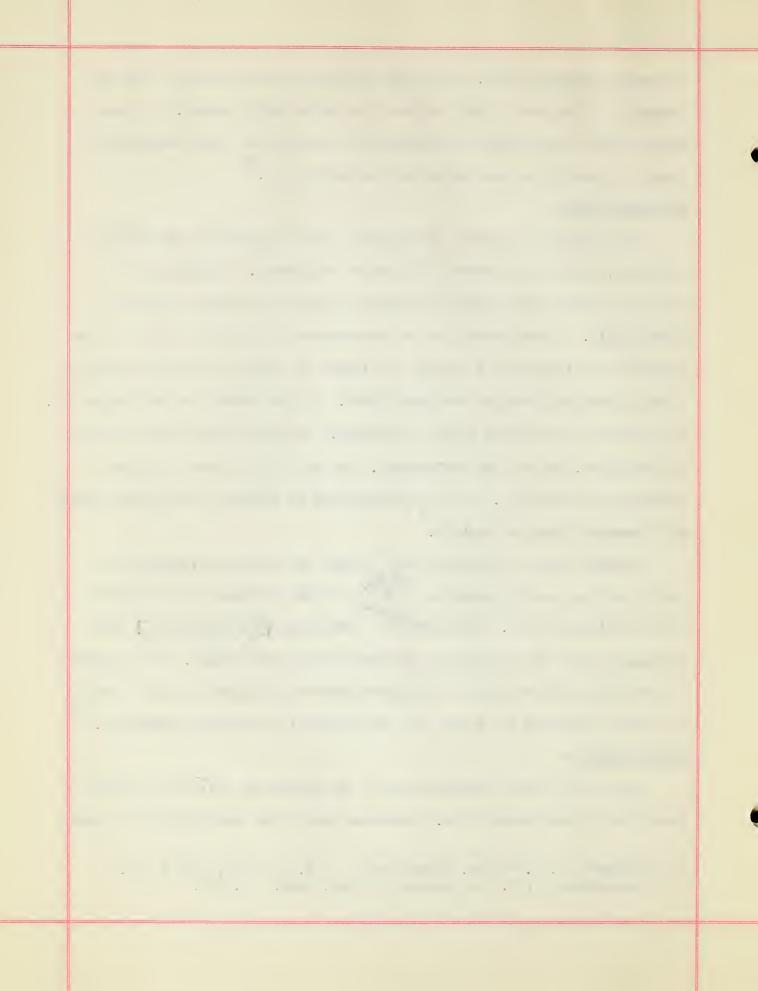
Another form of artificial silk is made by treating cellulose with cH<sub>3</sub>CO or in the presence of a catalyst such as sulphuric acid. The acetyl cellulose CH<sub>3</sub>CO cellulose CH<sub>3</sub>CO cellulose CH<sub>3</sub>CO cellulose CH<sub>3</sub>CO cellulose CH<sub>4</sub>CO cellulose CH<sub>4</sub>CO cellulose CH<sub>4</sub>CO cellulose CH<sub>4</sub>CO cellulose cellulose cellulose cellulose cellulose cellulose acetate and approaches more nearly to natural silk than any other, and the process is of growing importance.

Textile tests:-

One of the first considerations in the buying and selling of textile materials is their composition. There are people who consider that the term

<sup>10 -</sup> Kingzett, C. T. - Chem. Encyclopedia - P.P. 545, 997, 809, & 811.

<sup>4 -</sup> Chamberlain, J. S. - A Text-book of Org. Chem. - P. 364.



"woolen" may be interpreted as "wool-like" and so a "wool-like" fabric may be termed "woolen" although it contains no wool. Such descriptions are deceptive and will not be used by reputable traders. To be safe from fraud it is necessary for the buyer to know some simple textile tests for they will give more effective guidance than will appearance and handling.

The Table Figure 14 gives some simple tests for composition of 28 fabrics.

## PAINTS AND VARNISHES

#### Paints:-

Paints are mixtures of pigments with an unsaturated oil such as linseed oil or turpentine, and may be considered as composed of two parts, the pigment and the vehicle. The term pigment is applied to the insoluble, opaque coloring matter. The vehicle is the unsaturated oil with which the pigment is mixed.

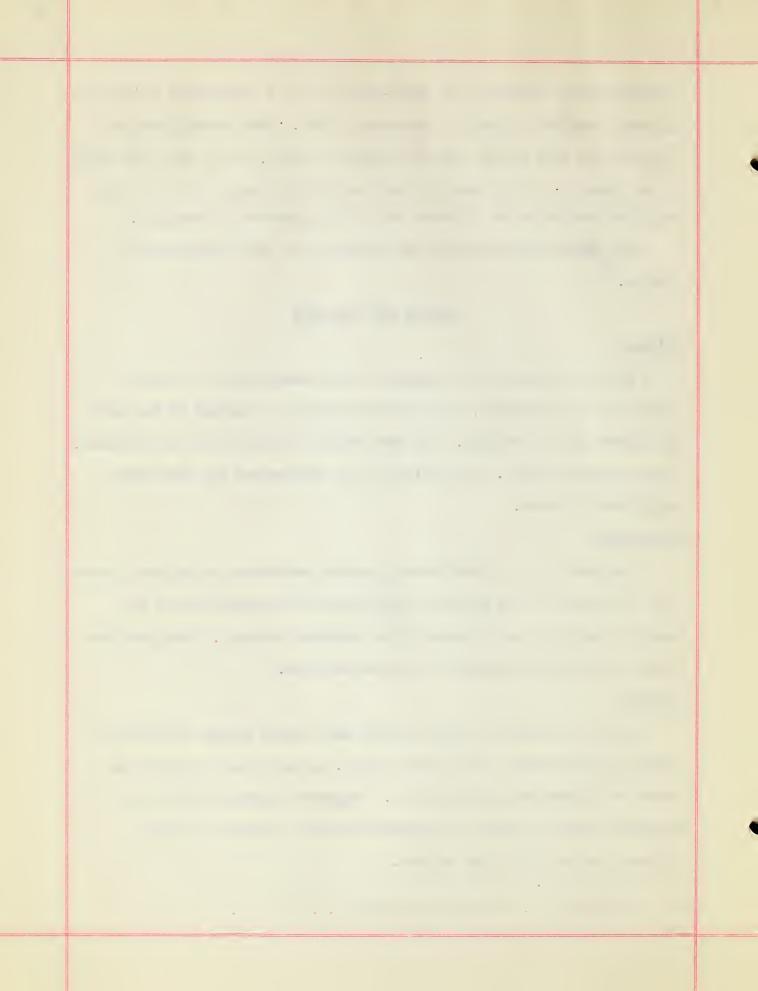
## Varnishes:-

Varnishes are the solutions of resinous substances which, when spread over the surface of any object, leave behind after evaporation of the volatile vehicle, a shiny layer of the dissolved material. Varnishes are used as protective coverings for various surfaces.

#### Driers:-

Driers are materials used in paint and varnish making to hasten the drying of the product after being applied. After making varnishes the driers are introduced and churned in. Manganese dioxide, cobalt and manganese oleates, cobalt and manganese borates, litharge, and zinc sulphate, are used for this purpose.

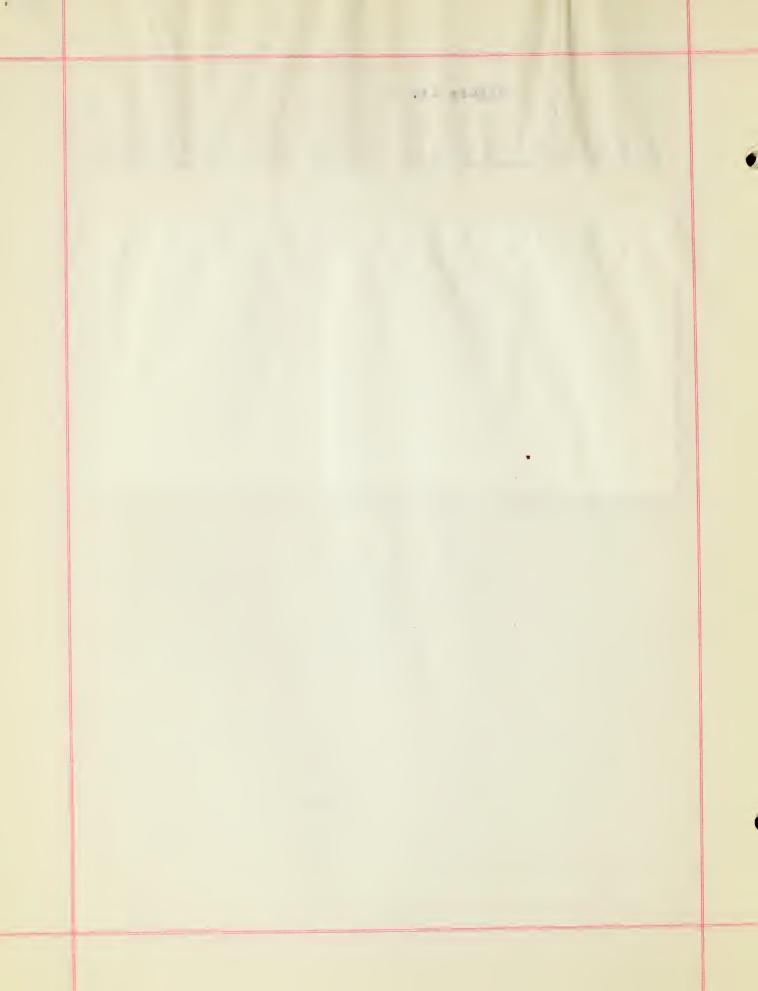
28 - Williams, J. G. - Textiles on Test - P.P. 5, 6 & 7.



# Figure 14.

# Simple tests for composition of fabrics.

1. Burn yarns extracted from the fabri	. There are three possibilities—	
Burns readily. After extinction fums smell of—     Burned paper, leaving light   or vineg grey ash.   leaving ble be a ds yarns.	fumes smell of burned feathers, soft black globules left.  leaves black showing origin	ash, the
Now apply second tests to fresh yarns-  2. Wet the yarns.  Retention Loss of of strength.  Loss of or acetic aci or aceton Becomes sticky.	chloric acid.  Dissolves in about five ninutes.  Does not dissolve. Boil in acid, lea only an ly brogelati.	hy- loric ving easi- ken
Cotton, Cellulose Acetate hempor rayon. rayon.	Unweighted Wool.  Unweighted Silk.  Does not dissolve. Wild silk.  Mine weigh silk.	ral



### Spirit varnishes:-

Spirit varnishes consist of gum shellac or other resinous substances dissolved in a suitable volatile solvent or mixture of solvents. The solvents used depend upon the application to be made of the products. Shellac:-

Shellac is an excretion of the lac insect which abound in tropical forests and constitutes the resinous covering on the branches of various jungle trees. Siam and India are the world's largest producers.

## Enamels:-

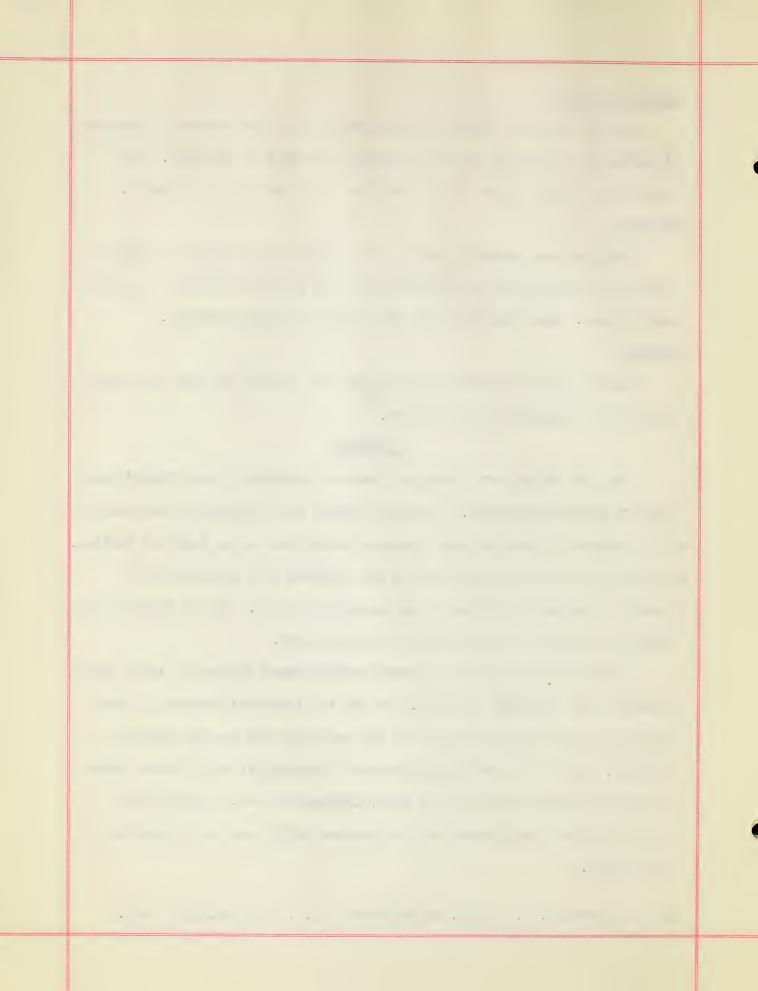
Enamel paints are those ready-mixed with varnish so that upon drying 10 they leave an enameled face or gloss.

### LACQUERS

The word "lacquer" is derived from the Hindustani word "lackh" which means "a hundred thousand". The name "lackh" was originally given because of the myriads of insects whose resinous secretions is the basis of shellac. Lacquering in the modern sense means the applying of a protective or ornamental finish to articles of wood, metal or fibre. At the present time artificial lacquers are being made from cellulose.

In the last few years an almost revolutionary change has taken place in the art of finishing surfaces. One of the important factors of this change has been the rapid spread of the knowledge and use of pyroxylin lacquers, and its successful application to automobile bodies where under a variety of trade names such as Duco, Lacqueroid, etc., it has become familiar to the high percent of the American public who are interested in automobiles.

10 - Kingzett, C. T. - Chem. Encyclopedia - P.P. 659, 950, 951 & 661.



By treating cellulose material with a mixture of nitric acid and sulphuric acid, a series of compounds can be produced which are termed nitro-celluloses. In the nitration process for the manufacture of the various nitro-cellulose products, whether pyroxylin, collodion, or gun cotton, is treated with the nitric acid and sulphuric acid mixture. The proportions and concentrations of the acids and the length of time and the temperature of nitration are definite for each product, and are determined by the degree of nitration desired.

### Pyroxylin:-

The term pyroxylin is generally used in designating the lower cellulose nitrates containing about 10.5% to 12.2% nitrogen. These cellulose nitrates are soluble in amyl acetate and in methyl alcohol and are used in preparing lacquers, celluloid, and in making artificial silk.

# Collodion cotton:-

Collodion cotton is a nitrated cotton product containing about 12% nitrogen and is used in the manufacture of silk substitutes and lacquers. Pyro-collodion:-

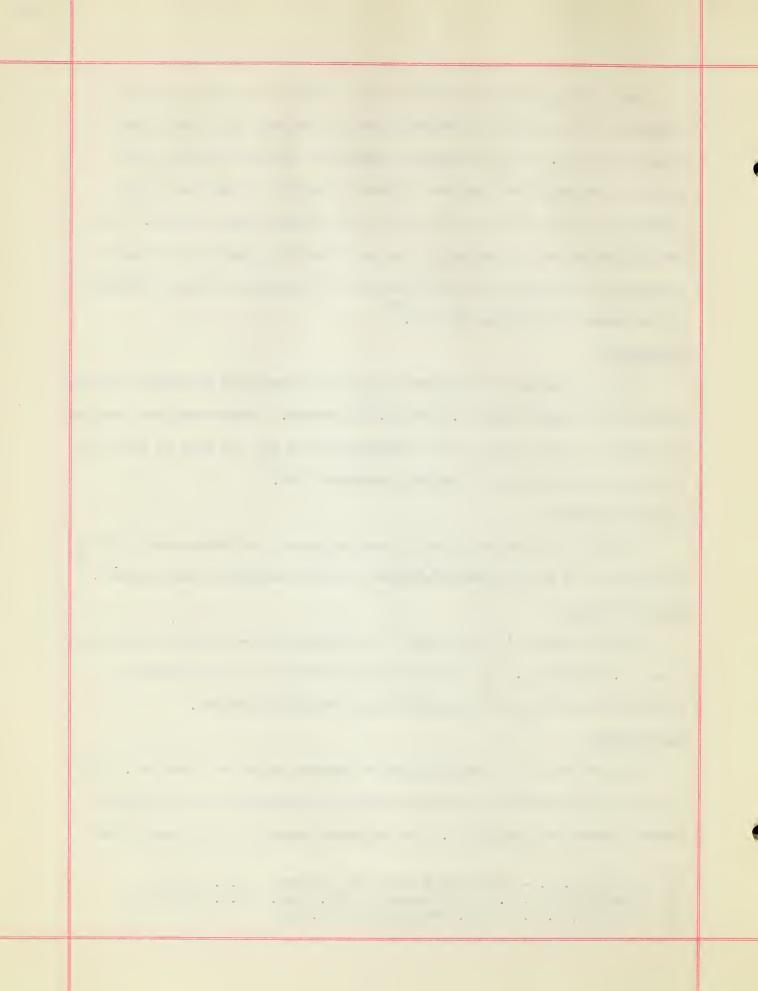
Pyro-collodion is a term used to designate nitro-cellulose containing about 12.6% nitrogen. It is more or less soluble in an alcohol-ether mixture, and is used in the manufacture of smokeless powders. Gun cotton:-

Gun cotton is a nitro-cellulose of maximum degree of nitration. This is practically insoluble in materials used in lacquers and is, therefore, useless except for explosives. The following reaction takes place in the

<sup>29 -</sup> Wilson, S. P. - Pyroxylin Enamels and Lacquers - P.P. 1 & 11

<sup>4 -</sup> Chamberlain, J. S. - A Text-book of Org. Chem. - P.P. 366 & 367

<sup>10 -</sup> Kingzett, C. T. - Chem. Encyclopedia - P. 222



complete nitration of cotton:-

$$C_{6}H_{10}O_{5} + 3 HNO_{3} \longrightarrow 3 H_{2}O + C_{6}H_{7}O_{2}(NO_{3})_{3}$$

Can cotton or Cellulose tri-nitrate

The sulphuric acid used in the manufacture of nitrated cotton serves 4 as a dehydrating agent.

#### Dopes:-

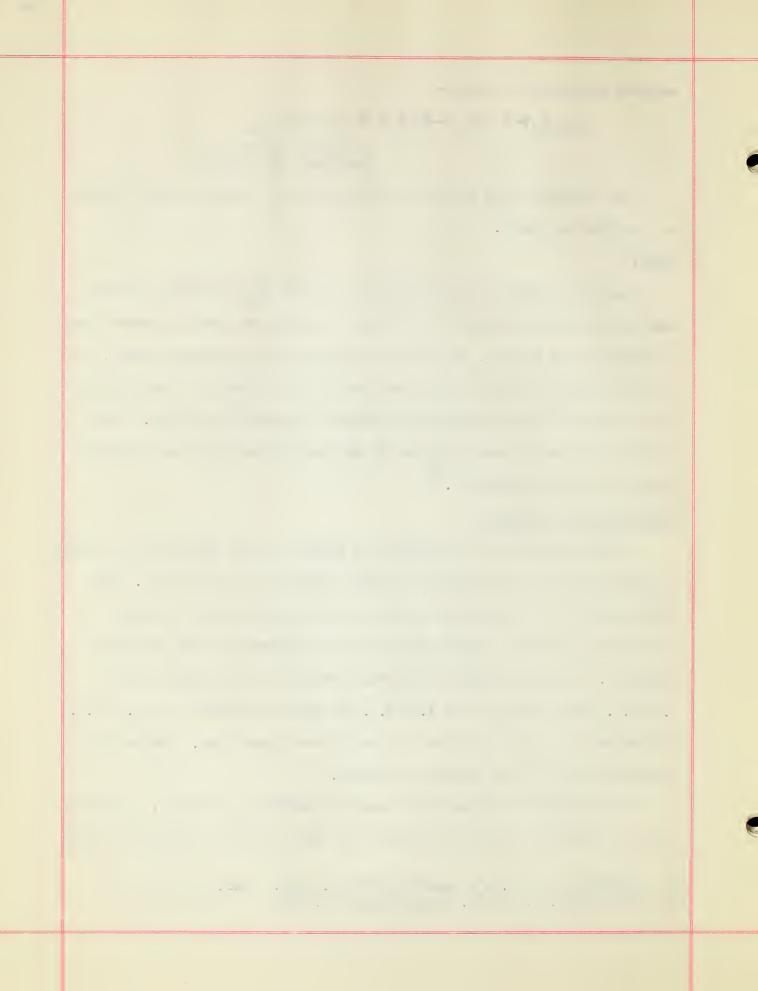
made by dissolving cellulose or cellulose compounds in certain solvents such as acetone, amyl alcohol, amyl acetate, butyl acetate or othyl acetate. A cellulose nitrate solution can be rendered fire resistant, by the addition of 5% to 3% of ammonium phosphate or ammonium magnesium phosphate. This qualifies nitro-cellulose solutions to compete with solutions of cellulose acetate as an air plane dope.

# Manufacture of pyroxylin:-

In the manufacture of pyroxylin, a typical charge consists of 32 pounds of cotton and about 1600 pounds of mixed sulphuric and nitric acid. The composition of the mixed acids must be carefully controlled as slight difference in content of acids may alter the properties of the resulting pyroxylin. A typical mixed acid formula consists of 20% nitric acid of 1.47 S.G., 40% nitric acid of 1.36 S.G. and 40% of sulphuric acid 1.84 S.G. The temperature of the solution is also of great importance. Temperatures between 35 and 55 C are generally employed.

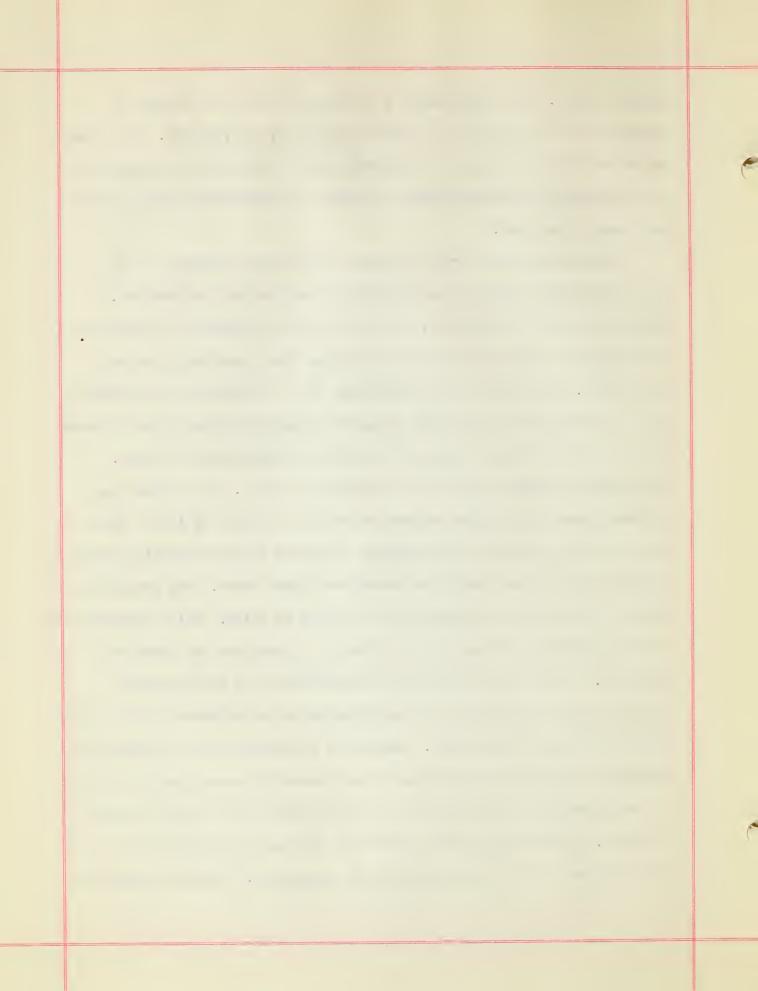
The cellulose is dumped into huge pots containing stirrers, so arranged that the cellulose is rapidly submerged and kept in motion through the large

<sup>4 -</sup> Chamberlain, J. S. - A Text-book of Org. Chem. - P.P. 366 & 367 10 - Kingzett, C. T. - Chem. Encyclopedia - P. 278



excess of acid. The large excess is required to avoid the change in composition of the acid due to amounts used up in the reaction. In a large amount of acid this change is negligible and the variation in composition of the pyroxylin which would occur, if only the calculated amount of acid were used, is avoided.

The reaction takes from 15 minutes to one hour depending on the type of pyroxylin desired, the temperature, and the acid composition. When the reaction is completed, the cotton and acid mixture is allowed to fall through a valve in the bottom of the pot into a centrofuge on the floor below. The acid is thus whizzed out in a few minutes and is pumped back to tanks where a calculated amount of string fortifying acids is added to it in order to bring it back to the desired concentration for use. The pyroxylin is next boiled with slightly acid water. The matted lumps are transferred to a pulping machine where they are beat up into a pulp. From the pulping machines the pyroxylin is placed in tubs and boiled with slightly alkaline water and then washed with fresh water. The pyroxylin is now pure, except for the presence of about 25% of water. This is undesirable for the manufacture of lacquers, as water is a precipitating agent for pyroxylin. On the other hand dry nitro-cellulose is a very dangerous substance and its transportation is forbidden by common sense as well as the Interstate Commerce Commission. Therefore, practically all the commercial pyroxylin is dehydrated by forcing alcohol under 300 pounds pressure through the wet pyroxylin, and the product as sold contains 30% of ethyl alcohol by weight. Since ethyl alcohol mixes well with most ingredients of a lacquer formula, it is not an undesirable ingredient. Lacquers consist of



pyroxylin dissolved in such solvents as acetone, amyl acetate, amyl alcohol.
29
etc. Pigments are mixed with the lacquer to give it color.

## EXPLOSIVES

### Snokeless powder:-

Gun cotton, when ignited in a gun barrel, burns very fast and is liable to detonate causing loss of life. However, danger of detonation can be avoided if the gun cotton is gelatinized. In the manufacture of smokeless powders, this is accomplished with a mixed solvent containing 40% acetone and 60% alcohol. The gelatinized gun cotton is suitable for use in the manufacture of smokeless powders and will not detonate.

# Nitro glycerine:-

Nitro-glycerine is formed by the action of nitric acid on glycerine.

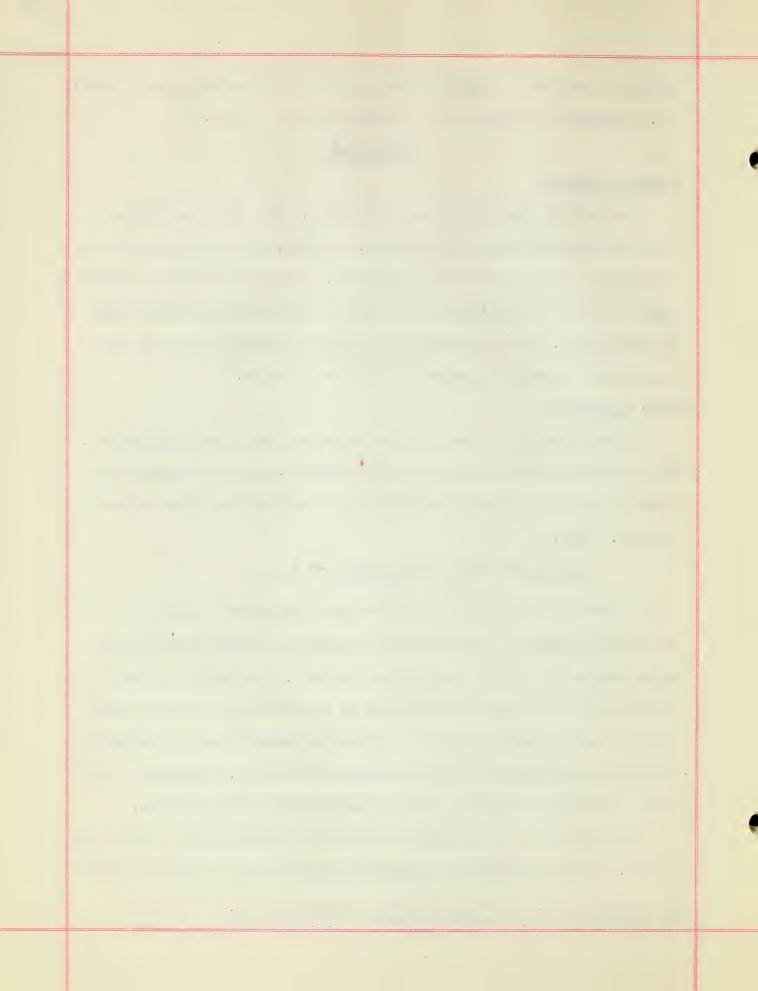
The formation of one molecule of nitro-glycerine requires one molecule of glycerine and three molecules of nitric acid, setting free three molecules of water. Thus:-

$$C_{3}H_{5}(OH)_{3} + 3 INO_{3} \longrightarrow C_{3}H_{5}(NO_{3})_{3} + 3 H_{2}O$$

However, if glycerine is added to such a calculated quantity of practically anhydrous nitric acid, the formation of nitro-glycerine soon ceases because the water formed dilutes the acid. For complete conversion of glycerine into glycerine tri-nitrate it is necessary to have an excess of nitric acid molecules and also a dehydrating agent which will maintain a sufficient concentration of the esterifying nitric acid. Sulphuric acid is used as the dehydrating agent in the manufacture of nitro-glycerine.

The nitration is carried on in cylindrical vessels made of either iron or lead. In the manufacture of nitro-glycerine the use of iron is avoided

29 - Wilson, S. P. - Pyroxylin Enamels & Lacquers - P.P. 13, 14, & 15 30 - Bernadov, J. B. - Smokeless Powder - P.P. 158 & 159

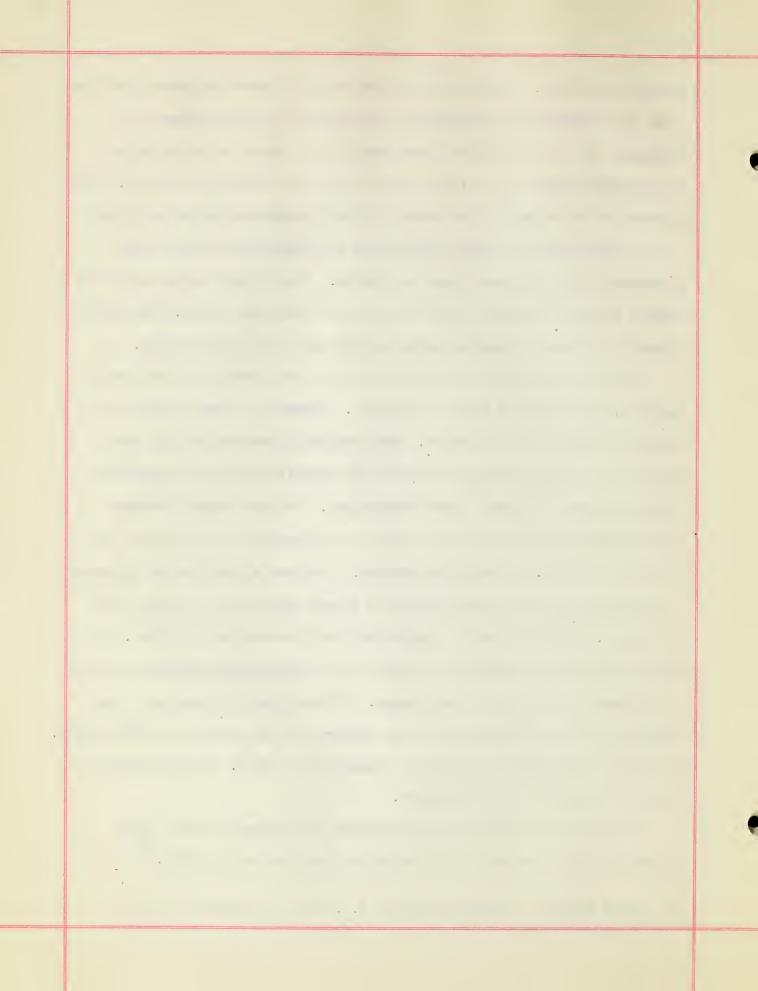


as far as possible, since in cases of explosion it forms dangerous missiles, while lead apparatus and accessories, on account of their softness and toughness, are for the greater part found at the center of an explosion as a crumpled mass and are less readily torn into far-flying missiles. The contents of the nitrators are mixed by rising compressed air which is lead in by a light lead pipe which distributes the compressed air into the apparatus a short distance above the bottom. The cylinder has a cover with windows inserted affording a good view of the reactions within. The mixture is cooled by means of cooling coils through which cold water passes.

From the acid tank the acid flows into a room where it is weighed or measured, and from here into the nitrator. Glycerine is next added to the mixture of acids in the nitrator. When feeding glycerine into the acid mixture it is very important to obtain the highest velocity of subdivision possible in order to avoid locat overheating. For this reason various distributers have been made which permit the glycerine to flow out on the surface of the acid in many fine streams. The rate of addition of glycerine is regulated by a valve maintained in a closed condition by a spring when not in use. When the hand is removed the valve automatically closes. The flow of glycerine is automatically shut off if the operator happens to leave the nitrator on account of some danger. The addition of glycerine is so regulated that the temperature of the mixture does not exceed a certain limit. It is never permissible to exceed a temperature of 50 °C. In many plants a temperature of 25 °C is not exceeded.

When the nitration has been completed the nitro-glycerine being 31 lighter floats on top and can be separated from the acid mixture.

31 - Maoum Phokion - Mitro-glycerine - P.P. 25, 54, 55, 56, 57 & 59



# Nitro-glycerine explosives:-

The chief nitro-glycerine explosives are dynamite, blasting gelatin, and gelatin dynamite. Dynamite is the name given to any explosive consisting of an ingredient holding nitro-glycerine in absorption. It is the most important and most frequently encountered commercial explosive manufactured in this country.

#### Dynamite:-

Dynamites consist of a mixture of from 15 to 60 percent of nitroglycerine and an active absorbent such as sawdust, sulphur, sodium nitrate,
calcium or magnesium carbonate.

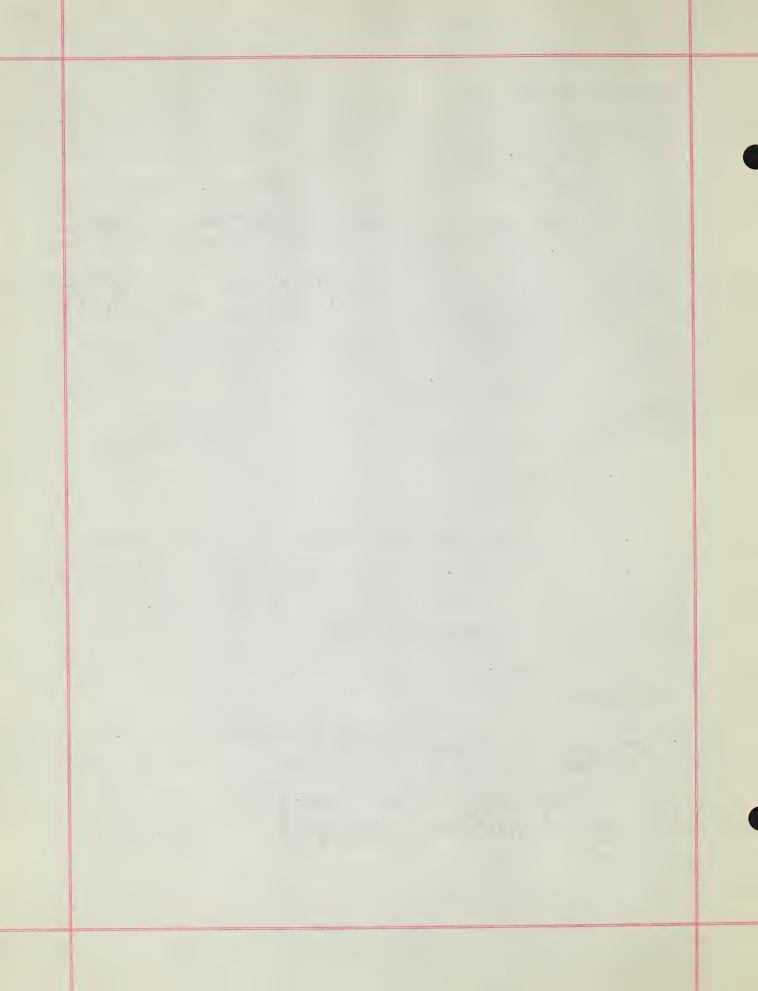
# Blasting gelatin: -

Blasting gelatin is a yellow, gelatinous mixture more stable than dynamite. It is usually made in 8 inch sticks,  $l_2^1$  inches in diameter and is composed of about 94 parts of nitro-glycerine and 6 parts of collodion cotton. It is the most powerful explosive known having a power twice that of T.N.T., weight for weight. When frozen it becomes extremely sensitive to shock and is, therefore, dangerous to handle in that condition. Not being affected by moisture, it is a valuable explosive for work under water and in other wet places.

# Golatin dynamites:-

Gelatin dynamites are used extensively as commercial explosives.

They are manufactured from nitro-glycerin to which is added from one to three percent of specially prepared cellulose nitrate. They are no more unstable than dynamite and are designated as 25% to 90% gelatin dynamites.



# Permissible emplosives:-

These are explosives which are used in coal mines or elsewhere in the presence of combustible gases. The temperature of the flame accompanying detonation will not ignite the mixture of gas and air. These explosives are composed of oxidizing salts as the base mixed with from 4% to 12% of nitro-glycerine. The nitro-glycerine increases the sensitiveness to 32 detonation and insures propagation of the explosion.

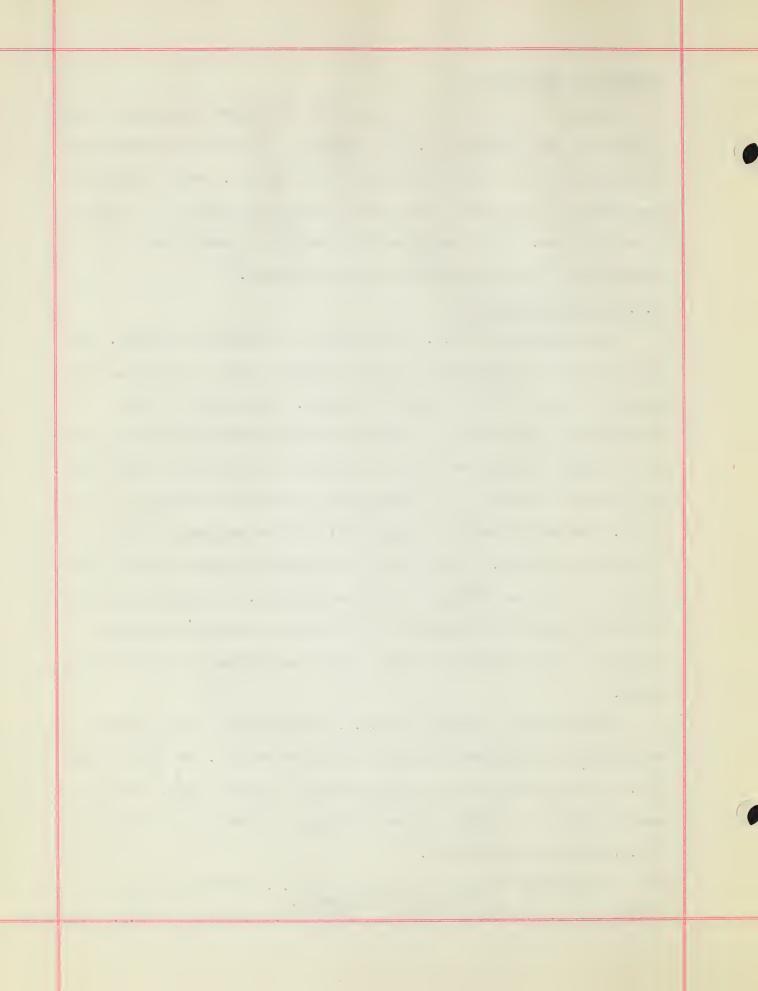
# T.N.T. (TRINITROTOLUENE):-

The manufacture of T.N.T. is a problem in temperature control. The first step in the manufacturing is the nitration which is carried on in a large cylindrical vessel called the nitrator. The nitrator is well equipped with cooling coils and heating coils so placed that the temperature of the reacting mixture responds instantly to the operation of these coils. The cooling is effected by the circulation of cold water through a set of coils. The heating coils are supplied with either superheated steam or steam under pressure. In addition to the temperature control coils, the nitrator is equipped with good agitating apparatus. The agitating apparatus is just as necessary as the water and steam coils, because keeping the mixture of toluene and acid uniform, aids in maintaining the temperature level.

Following the nitration the T.N.T. and spent acids are transferred to a separating pan where the charge is allowed to cool. On cooling, the T.N.T. crystallizes out and so separates from the spent acids. Water is usually added to the mixture in order to more completely precipitate the 53 T.N.T. from the acid solution.

<sup>32 -</sup> Government Printing Office, Washington, D.C. - Explosives and Demolitions - TR 195-30.

<sup>33-</sup> Smith, G. C. - Trinitrotoluenes, Their Mfg. & Properties - P.P. 29,50 & 42



application. It is insensitive and will not detonate even under strong pressure or severe blows. In small quantities it can be burned, but in large quantities, the heat generated will invariably raise the temperature to the detonating point. It can be successfully used for demolition work under water. Mercurric fulminate will not detonate untampes T.N.T. It can, however, be detonated by the use of tetryl caps.

#### Detonators:-

The two important detonators in use are fulminate of nercury and tetryl (tetranitromethylaniline).

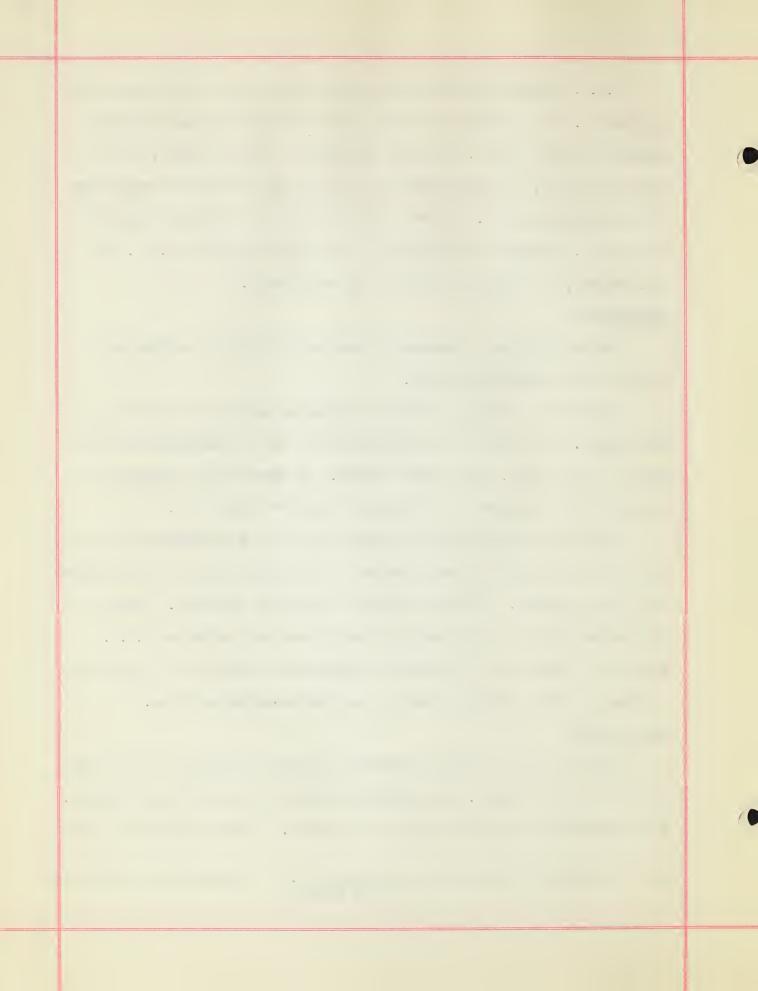
Fulminate of mercury is formed by treating mercury with nitric acid and alcohol. When pure it is yellowish white, but the commercial form is usually a gray color, due to free mercury. It shows unique properties as an initiator of detonation in other less sensitive explosives.

Tetryl is manufactured by a process involving the nitration of benzene, its reduction to aniline, the nitration of the aniline, and its combination with methyl alcohol. It can be detonated easily by hammering. Tetryl is an excellent initiator of detonation and is used for detonating T.N.T. One type of tetryl cap is composed of  $13\frac{1}{2}$  grains of tetryl and 7 grains of a mixture of 90% fulminate of mercury and 10% potassium chlorate.

#### Picric acid:-

Picric acid is a yellow crystalline explosive prepared by the action of nitric acid on phenol. When heated or struck it explodes with violence. It is insoluble in water and soluble in alcohol. Various mixture of it with

32 - Government Printing Office, Washington, D.C. - Explosives and Demolitions
TR 195-30



collodion in compressed form constitute the explosives melinite and lyddite.

10
It is also used as a yellow dye for silk or wool.

C H OH + 3 HNO  $\longrightarrow$  C H (NO) OH + 3 H O 6 5 Phenol or Picric acid or Carbolic acid. Trinitrophenol

#### PLASTICS.

#### Bakelite:-

When phenol ( ${\rm C_6H_5OH}$ ) is heated with formaldehyde a hard plastic mass known as bakelite is formed which has a variety of applications. Such materials are known as plastics and include in addition to bakelite certain 7 cellulose materials and artificial ivory.

#### Cellophane and artificial hair:-

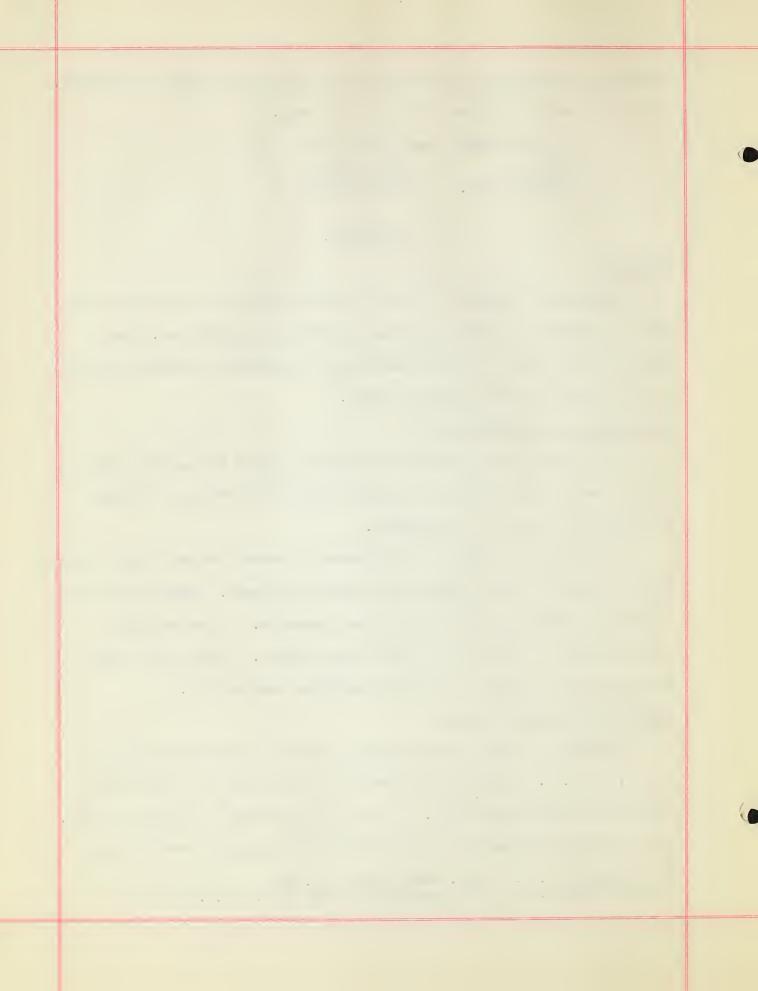
By forcing a thick solution of cellulose acetate and acetone through tubes of small bore, a kind of artificial hair can be produced, suitable for making hats and use in upholstery.

By changing the shape of the apertures, a straw like form can be made, and by widening the slit, ribbons or sheets can be made. Methods have been devised for making artificial lace in one operation. A thin wrapping material known as cellophane is made in this manner. Films used in the 10 motion picture industry are made from cellulose acetate also.

#### Artificial ivory from casein:-

Skimmed cow's milk is the principle source of casein and contains from 2.5 to 4.2%. Curdling is effected by the addition of a very dilute solution of hydrochloric acid. The curd thus produced is washed and dried. The casein thus produced is used in making plastics, jade, brush backs,

10 - Kingzett, C. T. - Chem. Encyclopedia - P. 705 7 - Williams, R. J. - An Introduction to Org. Chem. - P.P. 84 & 85



buttons, etc. A plastic, serving as a substitute for ivory, is prepared by moistening casein in 25% of water in which it swells, and is then forced into the shape of rods which can be rolled out in sheets. The casein is hardened lo by placing in a bath of 10% formaldehyde.

#### CHEMISTRY IN AGRICULTURE

Animal life could not exist without the oxygen of the air. In breathing, the oxygen is absorbed in the lungs and reacting upon the blood forms carbon dioxide which is given out in the breath. The inert nitrogen which is present in the air is of no direct use, but makes the oxygen dilute enough for the sustaining of life. Pure oxygen is fatal to human life when continuously breathed. The quantity of oxygen needed is so great that unless there existed some compensating process, life, in the course of time, would become impossible on the earth. Plant life gives back to the atmosphere the oxygen which animal life removes from it. Vegetable life absorbs carbon dioxide from the air, assimulates the carbon in its tissues by a variety of chemical processes and then gives back the oxygen content to the atmosphere. From all appearances the synthesis of the sugar found in the green leaves of plants takes place in sunlight with the aid of chlorophyl (C<sub>55</sub>H<sub>72</sub>O<sub>5</sub>H<sub>4</sub>Mg), the green coloring material in plants.

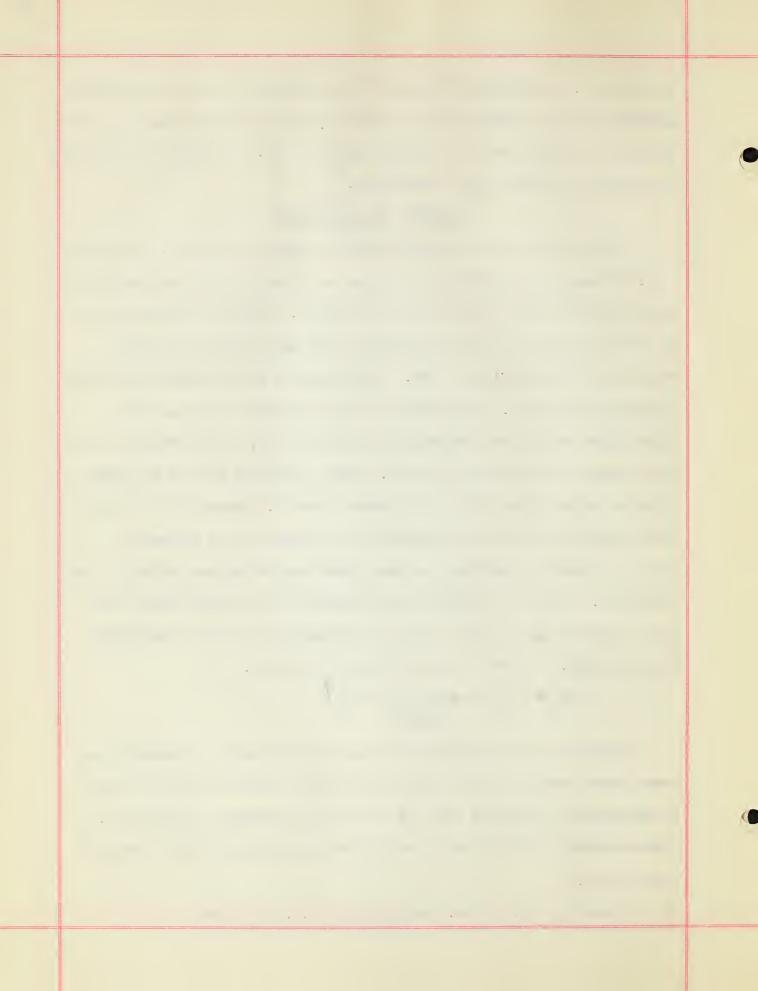
$$\begin{array}{c} \text{6 co}_2 + \text{6 H}_2 \text{0} \longrightarrow \text{c}_6 \text{H}_{12} \text{0}_6 + \text{6 o}_2 \end{array}$$

Vegetation has an important bearing upon the health of communities.

Trees absorb from the soil a great deal of water, which for the most part is subsequently evaporated into the air from the surfaces of the leaves.

Many malarious districts can be made drier and more healthful by means of plantations.

10 - Kingzett, C. T. - Chem. Encyclopedia - P.P. 812 & 150



#### SOILS:-

By soil is meant the outer crust of the earth consisting mainly of various mineral matters, resulting from the action of air, water, and other agencies upon rock, mixed with organic substances derived from the decay of vegetable growths.

The chemical constitution of soils varies according to the nature of the rocks from which they have resulted. Soils formed from the decomposition of limestone are not likely to be sour, but may be deficient in potassium. Soils formed from the decomposition of granite contain clay and are not likely to be deficient in potassium because granite contains potassium aluminum silicates. Sandy soils or soils derived from sandstone are poor for agriculture.

#### Acid soils or sour soils:-

Acid soils are infertile to most crops, but the acidity can be removed by liming. The addition of chalk or lime to the soil neutralizes it and makes it slightly alkaline which favors the action of nitrifying bacteria which develope abundantly in slightly alkaline soil.

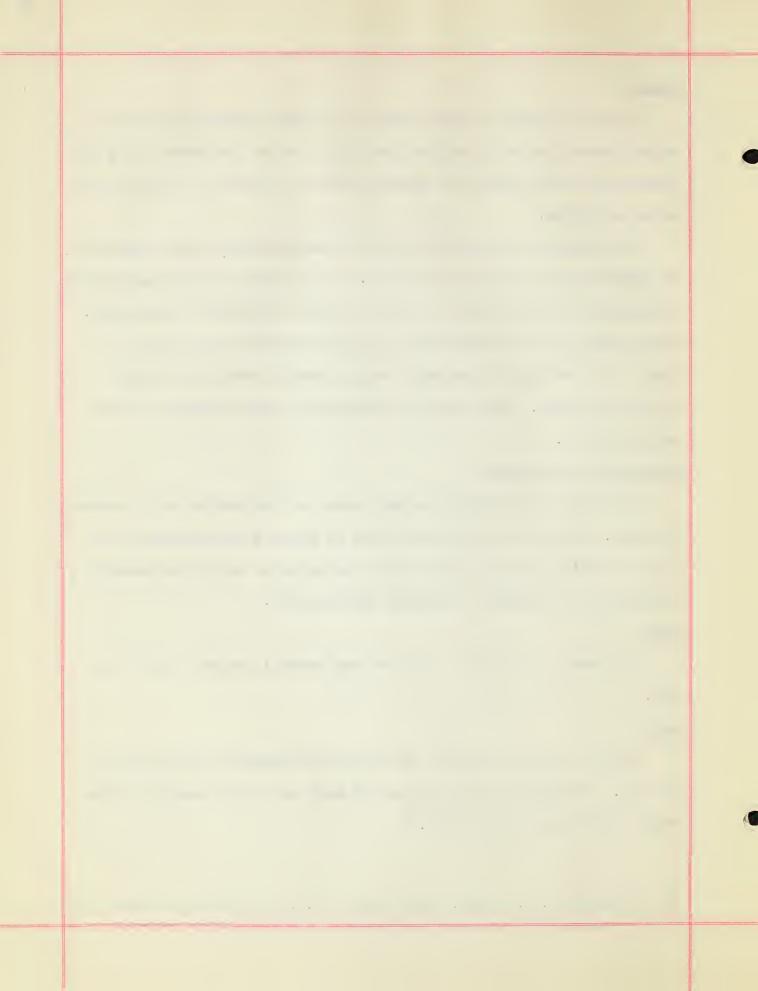
#### Loan:-

Clay more or less mixed with sand and vegetable matter is known as loam.

#### Humus:-

Humus is decayed vegetable matter and constitutes the black part of the soil. It contains a substance called humic acid which decomposes into 0 10 carbon dioxide and water at 80 C.

10 - Kingzett, C. T. - Chem. Encyclopedia - P.P. 14,15,953,838,839,548 & 450



#### The importance of water to plant life:-

Since plant food must be in solution in order to pass through the cell walls of the roots of plants, enough moisture must be present to dissolve enough material for the needs of the plant. There must also be enough water to circulate these solutions up through the plant, and replenish the water which evaporates from the leaves, keeping them cool in warm weather.

#### FERTILIZERS;-

The need of nitrogen in crop production cannot be overcmphasized. The lack of a plentiful supply of this element in organic form will inevitably make the land infertile. While 4/5 by volume of the atmosphere is nitrogen, most plants are powerless to extract it from the air. Certain bacteria that exist on decaying organic matter have the power of "fixing" atmospheric nitrogen in such combination that it will become available to plants. A large amount of atmospheric nitrogen is "fixed" by means of bacteria that exist in union with leguminous plants. These bacteria form nodules on the roots of the plants which they infest as shown in Figure 15, the plants furnishing food for the bacteria, while the bacteria take nitrogen from the air and convert it into such form that the plants can use it in the construction of their tissues. Legumes are nitrogen containing plants and are important in crop rotation. The cultivation of domestic legumes such as clover, alfalfa, peas, beans and peanuts cannot be urged too strongly. Certain sections of the country make use of these crops in rotation to furnish their nitrogen supply. For specialized crops, such as cotton, tobacco, and sugar cane, it is necessary to make additional use of nitrogen derived from a convercial source. However it is recombended that

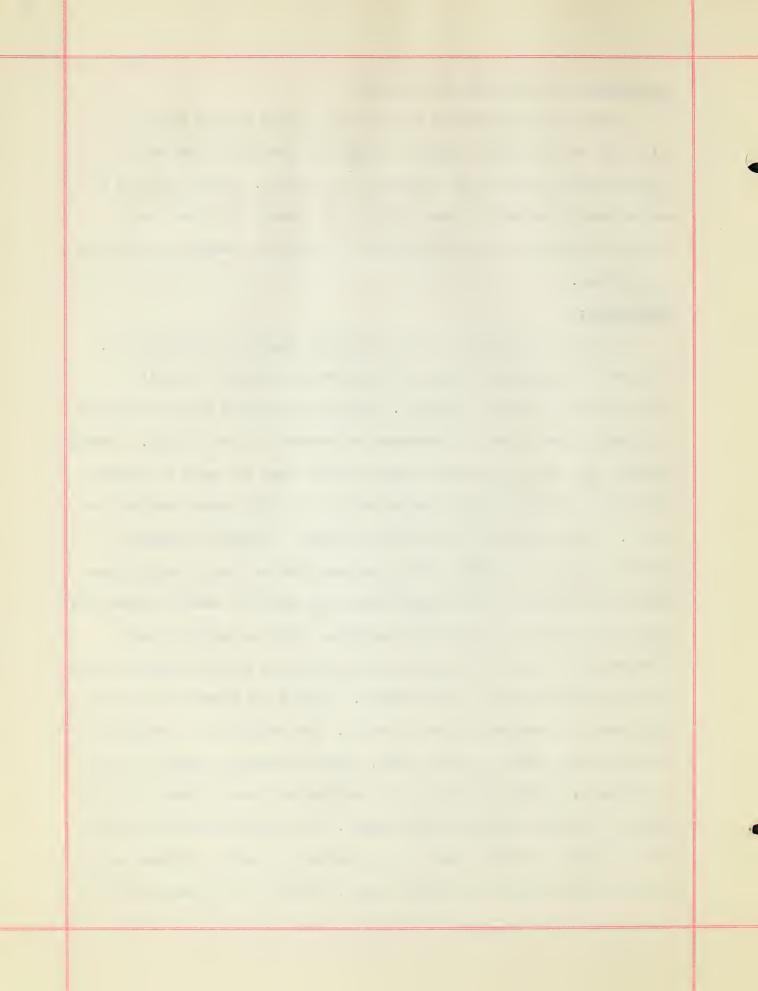
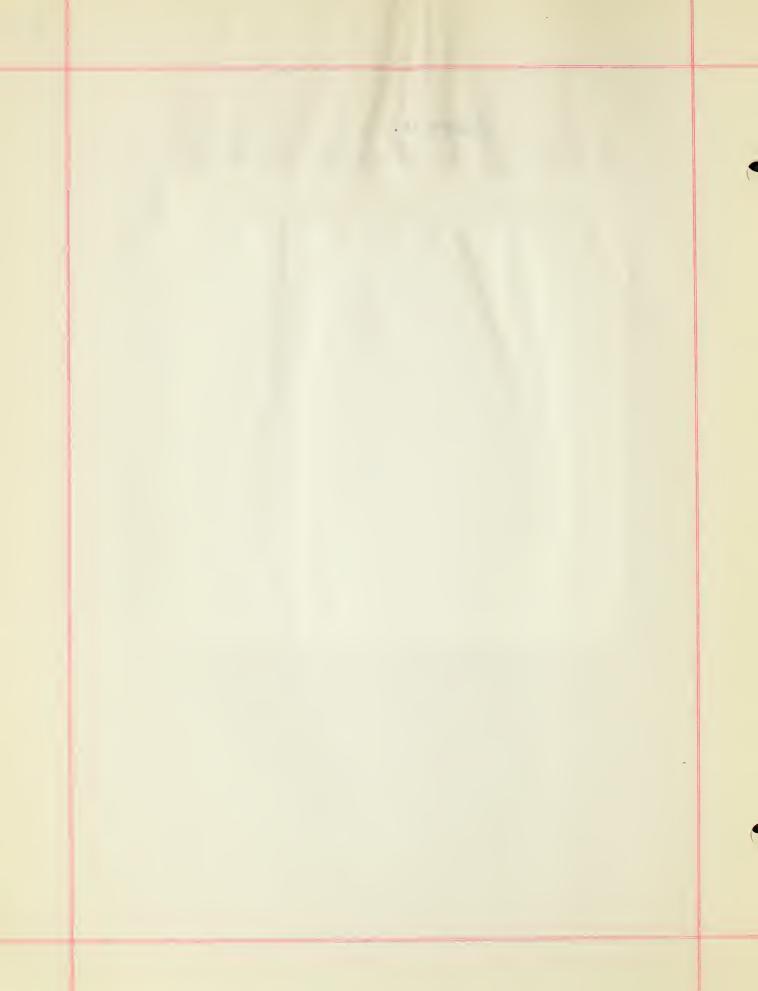


Figure 15.



196 9.—Roots of red clover showing nodules by which nitrogen is seeured for the plant.



the legumes be used to furnish a part of the nitrogen supply which is needed.

#### Phosphorous:-

When the soil is deficient in phosphorous content, it is necessary to make applications of it in commercial form. It is a constituent of the bones of animals, which are composed in part of calcium phosphate.

Phosphorous has an important part to play in the formation of the seeds of 34 plants and in hastening their maturity.

#### Potassium: -

Potassium in the soil favors the formation of carbohydrates, such as starches, sugars, and cellulose in the plant. It induces the healthy development of the leaf and stalk.

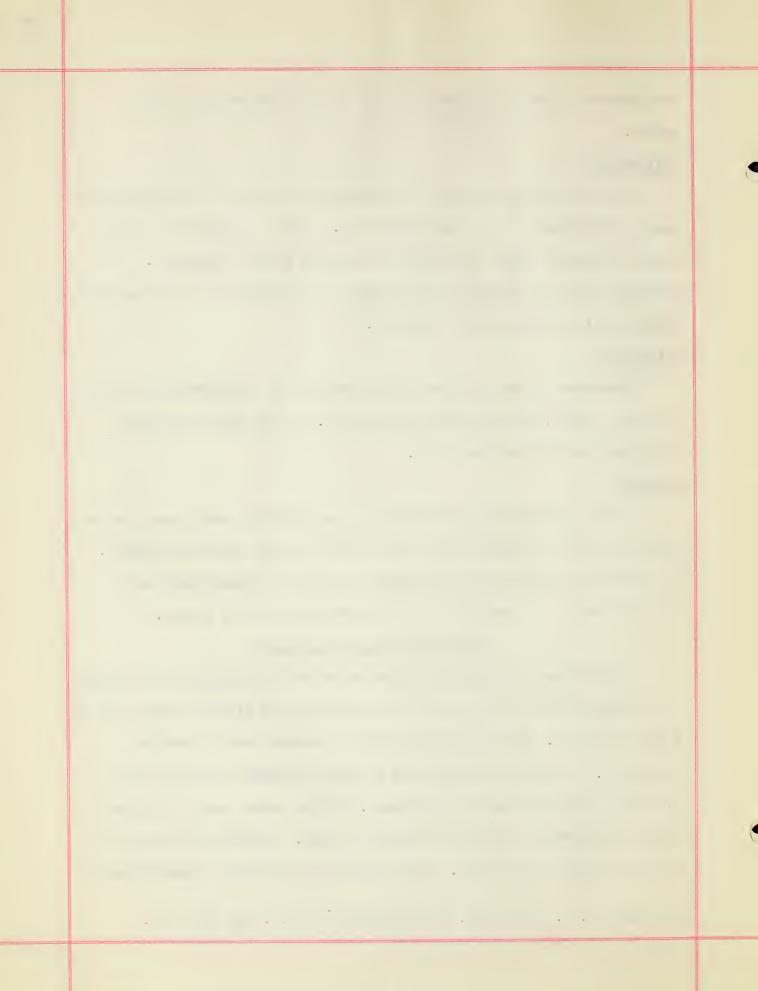
#### Nitrates:-

A large part of our nitrates used in agriculture today come from the nitrate fields of northern Chile in the form of Chile saltpeter (NaNO<sub>3</sub>). The commercial fixation of atmospheric nitrogen will undoubtedly be a valuable source of nitrogen for use in fertilizers in the future.

#### Insecticides and Fungicides

Insecticides and fungicides have to be used with discretion according to the known habits of the pests to be destroyed and with due regard for the safety of plants. Some insecticides hill by poison that is absorbed internally. Contact poisons have to be used on insects that such their food from the liquid contents of plants. In the latter case the insect is killed by absorbing the poison through his body. Insecticides are for the most part used in spray form. Many phenolic and creosotic preparations can

34 - Keit, T. E. - The Chem. of Farm Practic - P.P. 120, 122 & 38.



be employed for general use when properly diluted.

The ordinary arsenical weed-killers are made by dissolving proportions of arsenious oxide in sodium hydroxide solution.

A spray of lead arsenate is used for the destruction of fungoid growths and various kinds of noths on trees.

Hydrocyanic acid (HCN), applied by way of funigation is used to exterminate red spiders and certain fly pests in glass houses.

Calcium Arsenate is used for the destruction of the leaf worm and boll-weevil on growing cotton plants.

Copper sulphate in dilute solution can be used as a spray for mildows and insect posts on fruit trees and potatoes.

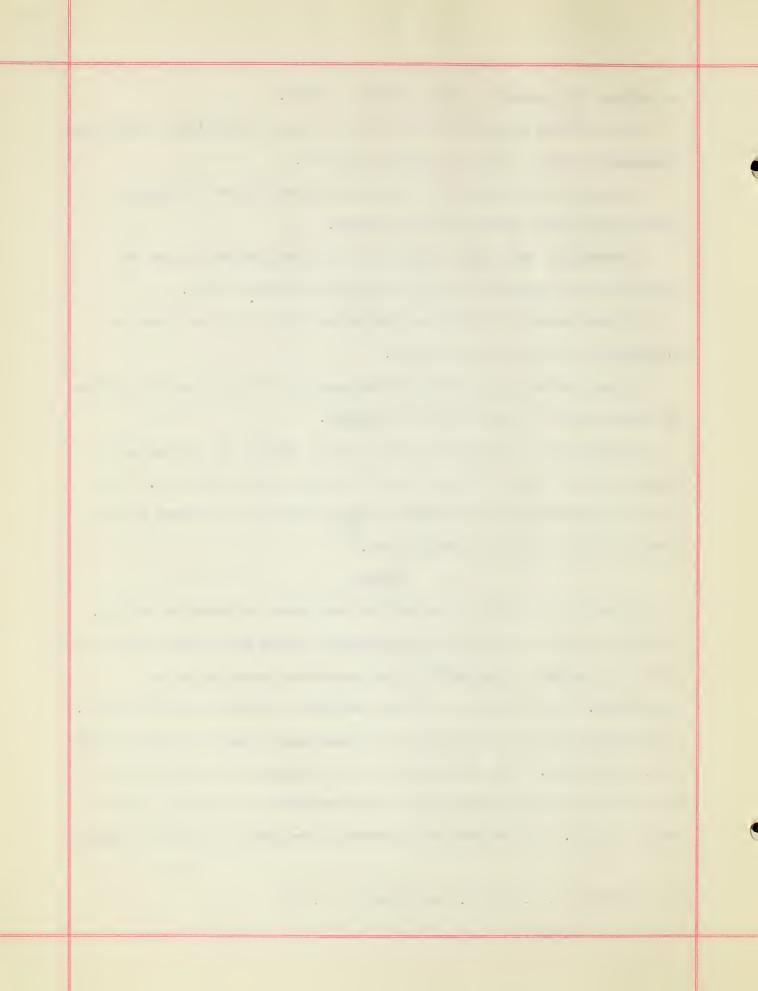
Paris green is prepared by adding sodium arsenate to a solution of a copper salt, and then treating the solid product with acetic acid. When used as an insecticide it is either sprayed in solution or dusted on the loaves are wet with dew.

#### RUBBER

Rubber is the juice of certain tropical trees collected by tapping.

The rubber juice or latex has a consistency of thick cow's milk or cream and exhibits a tendency to coagulate in the collecting cups during its procurement. To prevent this a dilute solution of sodium sulphite is used. The collecting cups for the latex are usually made of glass, glazed earthenware, or aluminum. When the latex has been collected the coagulation can be effected by adding acetic acid in the proportion of one part in 1000 parts of latex. This proportion is generally employed as the best coagulant.

10 - Kingzett, C. T. - Chem. Encyclopedia - P. 480



when the latex contains 3 pounds of rubber per gallon of latex.

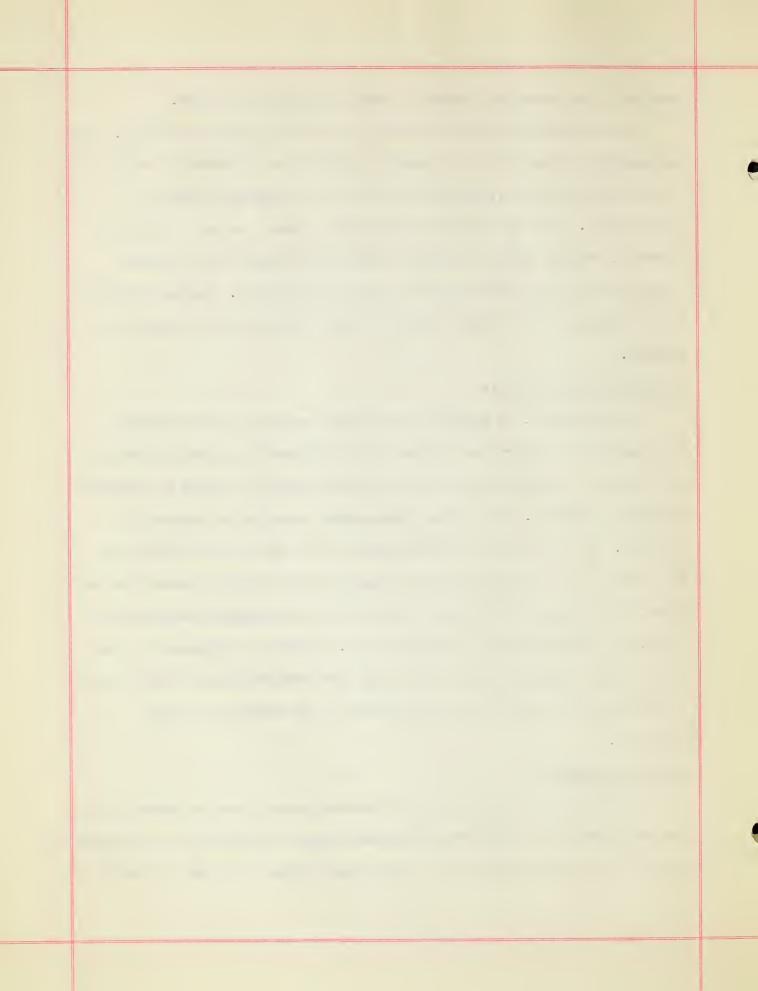
The coagulated rubber is prepared in the form of crepe or sheet. The wet coagulum is masticated and washed in mills, and subsequently rolled out into ribbons or sheets, thus getting rid of the water and soluble constituents. The long sheets of wet crepe of sheet are next dried in a darkened, well-ventilated, chamber, during which period the whiteness disappears, and the rubber takes on a pale yellow color. Sodium bisulphite is extensively used to bleach crepe or sheet rubber when this result is desired.

#### Vulcanization of rubber:-

Vulcanization, as ordinarily conducted, consists in the admixture (by kneading) of sulphur and various "filling" materials, such as zinc and lead oxides, and subjection of the resulting mixture to a heat of 130-140 °C under some pressure. At a higher temperature vulcanite or abonite is produced. In the process of vulcanization, the rubber is masticated and made plastic by steam heated rollers, one of which revolves faster than the other, after which, the materials required to give hardness and color are added, the sulphur being incorporated last. Rubber so vulcanized is less plastic than ordinary rubber, but retains its character over a better range of temperatures, and is not so susceptible to the action of various chemicals.

#### Artificial rubber:-

The production of artificial rubber was accomplished in Germany during the World War and was made from butadiene ( ${\rm C_4H_6}$ ), by placing it in hermetically sealed barrels and allowing it to remain undisturbed for about six months at



a temperature of 32°C. In this process the rubber is obtained as a spongy white mass which has to be bored out of the containers. This synthetic rubber, as at present made, is deficient in the physical properties of the natural article. It is useful in making so called vulcanites, but lacks clasticity when used in making soft rubber goods.

A new synthetic rubber named "Duprene" has been developed by E. I.

Du Pont de Nemours & Co., requiring only acetylene, salt, and water as raw
materials. It is claimed that this new synthetic rubber can be vulcanized
by the application of heat alone. More research will be required before the
product becomes profitable commercially.

Chemically rubber has until recently been regarded as a hydrocarbon  $(c_{10}H_{16})$  allied to terpentine  $(c_{10}H_{16})$ , but a later investigation shows that it may have a constitution represented by  $(c_{10}H_{10})$ .

#### CHEMISTRY IN HEDICINE

The discovery of many substances possessing either therapeutic power or the property of giving relief from pain is one of the great triumphs of the application of chemistry to medicine.

#### ANAESTHETICS, HYPNOTICS, HARCOTICS.

#### Substitution products of methane:-

The narcotic action of chloroform is closely connected with the amount of chlorine it contains. The entrance of chlorine into the molecule of many aliphatic compounds confer narcotic properties upon the substances formed. This fact is illustrated by the following series of compounds:-

CH, Methane

Without narcotic effect.

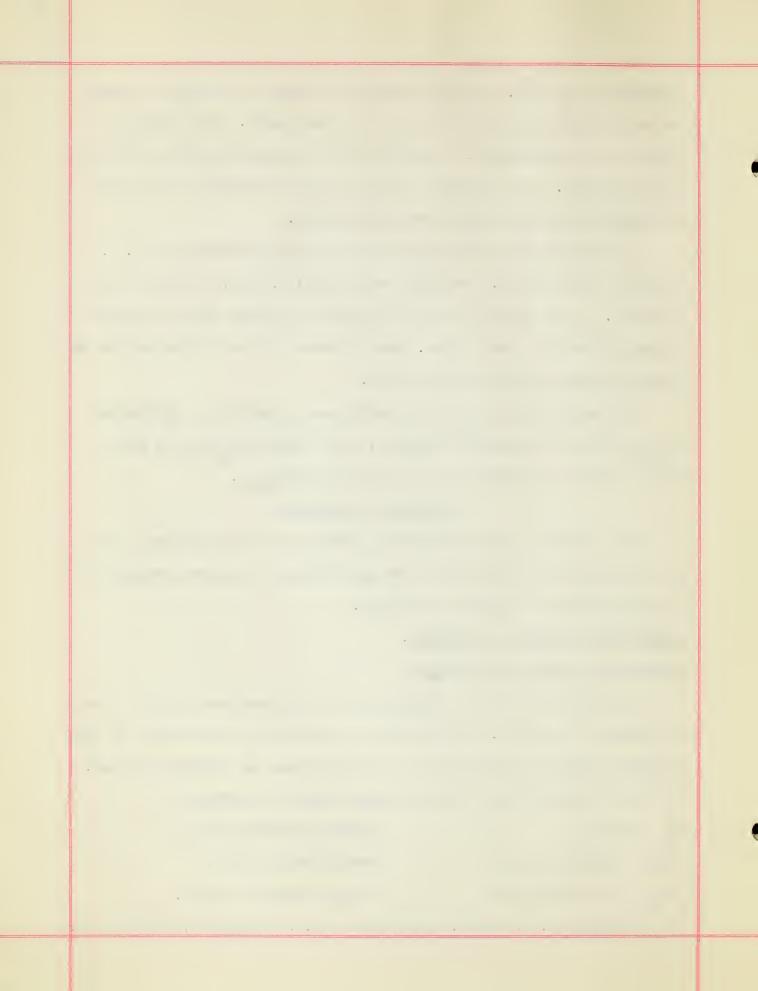
CH3Cl Methyl Chloride

Weak narcotic effect.

CH\_Cl\_ Dichlormethane

Stronger narcotic effect.

10 - Kingzett, C. T. - Chem. Encyclopedia - F.P. 767,768,769,773,777 & 771.



CHCl Chloroform

Strong narcotic effect.

CCl, Carbon Tetrachloride Strong narcotic effect.

In this series the intensity and persistence of the action increase with the amount of chlorine entering the molecule by substitution. Although carbon tetrachloride appears to have a stronger narcotic action than chloroform it has no advantages over it. As a matter of fact carbon tetrachloride seems too toxic for safe use.

## Chloral (CCl,CHO) and Chloral hydrate (CCl,CH(OH)):-

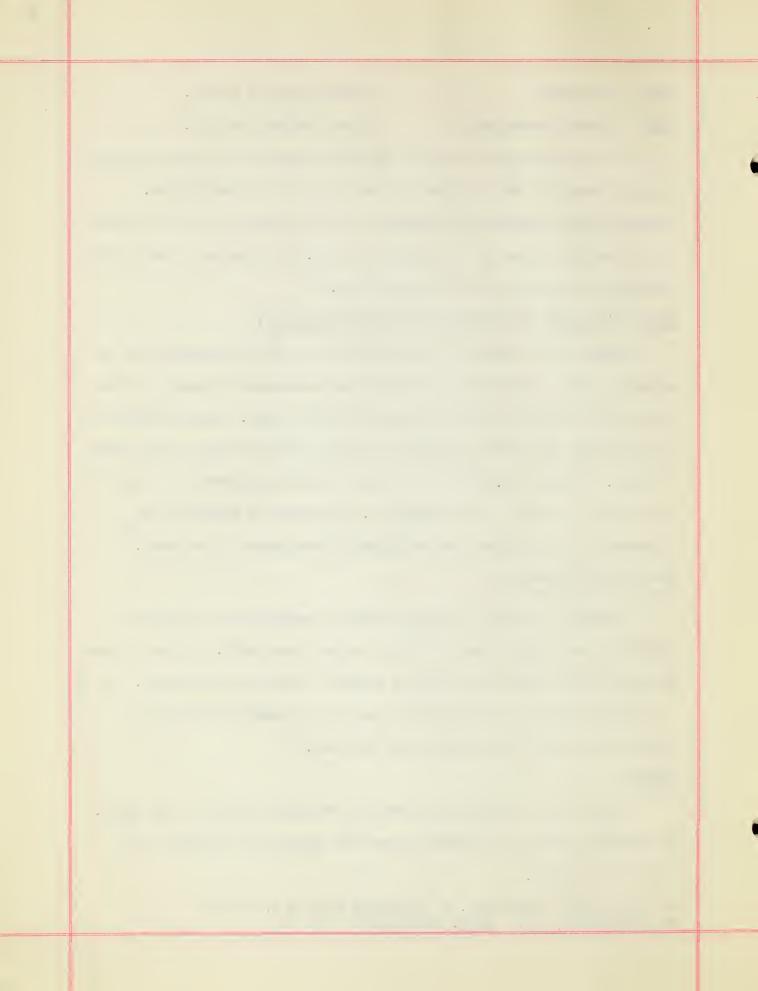
Chloral is a colorless liquid soluble in alcohol and ether and is prepared by the chlorination of alcohol and subsequent treatment of the product with sulphuric acid, followed by distillation. Chloral hydrate is a crystalline solid and is prepared by mixing chloral with a small amount of water. Although chloral was the first artificial hypnotic to come into general use, it suffers some drawbacks. It cannot be injected subcutaneously like morphine, and has harmful by-effects on the heart. Chloretone (C,H,OCl,):-

Chloretone is made by adding potassium hydroxide to a mixture of chloroform and acetone, and is a white crystalline solid. It has a great advantage over chloral in having no irritant action on the stomach. It is a sedative as well as an anaesthetic and very favorable results have attended its use in sea sickness and vomiting.

#### Opium:-

Opium is the dried juice extracted from seed vessels of the poppy. It contains a number of compounds known as alkaloids, including about 10-18% of morphine.

22 - May, Percy - The Chem. of Synthetic Drugs - P. 50, 54 10 - Kingzett, C. T. - Chem. Encyclopedia - P. 182



# Morphine (C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>. H<sub>2</sub>O):-

Morphine is a powerful drug extracted from opium, and is used medicinally as a sporific for the relief of pain.

# Cocaine (C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>):-

Cocaine was discovered in coca leaves in 1860. It had long been known that the South American Indians were in the habit of chewing these leaves as a stimulant to enable them to stand great exertion without fatigue. It is a colorless crystalline substance, soluble in water and alcohol and used as a local anaesthetic in operations.

#### Ether:-

10

The anaesthetic property of ether has been previously mentioned.

#### ANTISEPTICS

# Methylene blue (C16 H12 H3SC1):-

Methylene is an organic dye that is used internally for a variety of conditions, one of which is rheumatism.

# Hexamine ( (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>):-

Hexamine is a white crystalline substance soluble in water and alcohol. It is used as an internal disinfectant for the urinary system, the acid of the urine converting it into formaldehyde. It was used in gas 22 masks during the World War as an absorbent for phosgene.

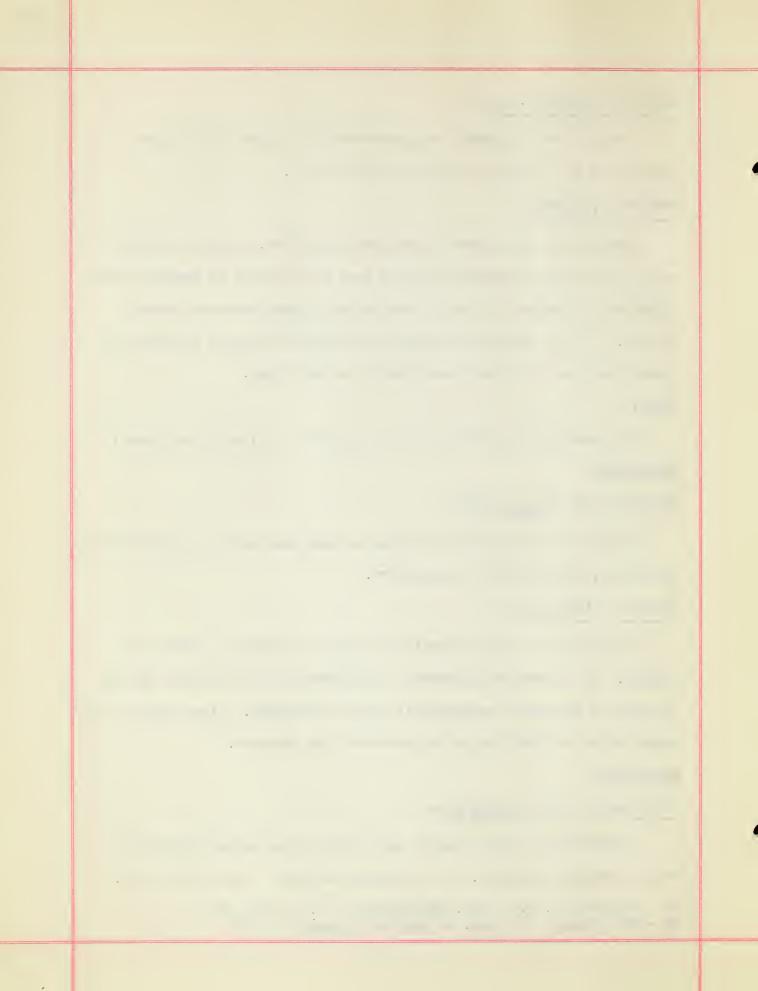
#### PURGATIVES

### Chrysophanic acid (C30H2607):-

Chrysophanic acid is one of the milder of the natural purgatives, and is present in rhubarb. It is soluble in water, alcohol and ether.

10 - Kingzett, C. T. - Chem. Encyclopedia - P.P. 640 & 218

22 - May, Percy - The Chem. of Synthetic Drugs - P. 171



Chrysophanic acid is used in unction form in cases of ring worm and other skin infections.

#### Jalap:-

Jalap is the dried root of the plant "Ipomoea purga" which grows in Tampico, Mexico, and is cultivated in Jamaica and India. It contains about 10% Jalapin ( ${}^{\rm C}_{34}{}^{\rm 65}{}^{\rm 0}_{16}$ ). This resin constitutes the powerful purgative. Croton Oil:-

This oil is one of the most powerful purgatives known and is obtained from the seeds of "Croton Tiglium", a tree cultivated in Southern Asia and China. It is soluble in alcohol and other and contains an oily substance named crotonol  $(C_9H_1O_2)$ , to which it owes its drastic purgative property and its irritating action on the skin.

#### QUININE

Quinine (C H H 0.5H 0) is a white crystalline solid extracted from the bark of cinchona trees and is soluble in alcohol, ether and is intensely bitter. The therapeutic value of quinine in the treatment of marlaria arises chiefly from the fact that it is more poisonous to the paracites 10 than to the cells of the host.

The following is a list of some of the terms used in the medicine with their meanings:-

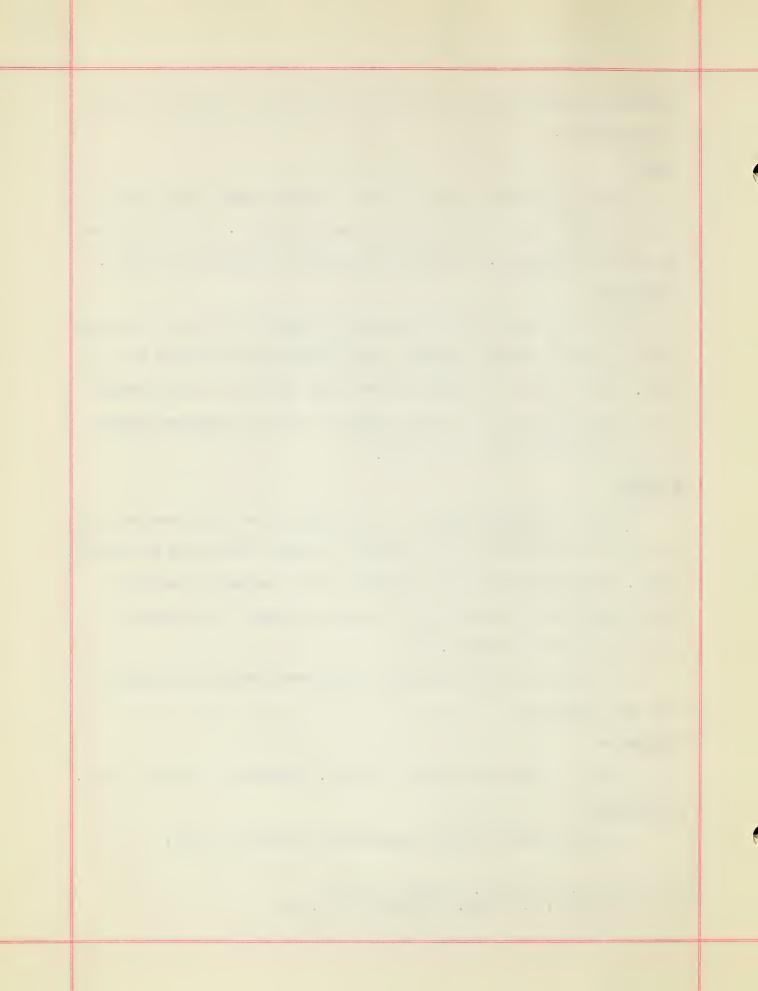
#### Sedative:-

An agent lessening functional activity. Possesses a quieting action.

Anaesthetic:-

A substance which produces insensibility to touch or pain.

38 - Evers, N. - The Chem. of Drugs - P. 172 10 - Kingzett, C. T. - Chem. Encyclopedia - P. 193



#### Narcotic:-

A drug that produced narcosis. Narcosis is the state of complete unconsciousness produced by a narcotic or an anaesthetic.

#### Hypnotic:-

A remedy that causes sleep.

#### Therapeutic:-

Curative.

#### Sporific:-

Producing sleep.

#### Unction: -

An anointment. Unctious means greasy or oily.

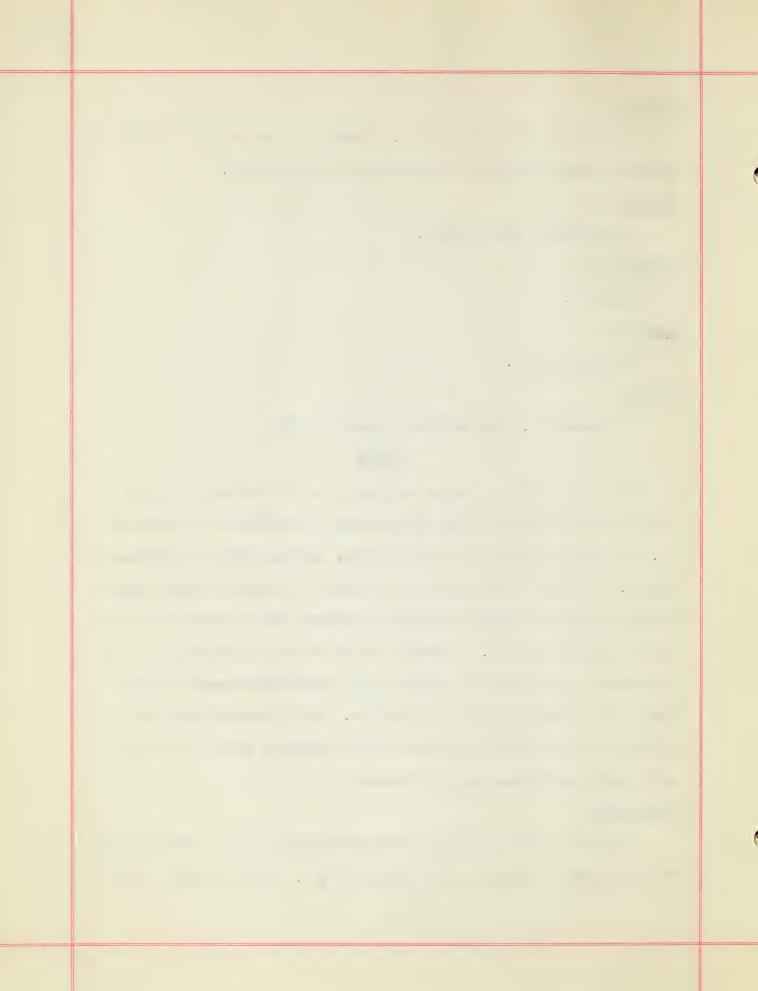
#### FOODS

The body is like an engine and must have fuel to keep it going.

"The fuel which keeps the body engine going is supplied in the food we eat. But besides keeping the engine going, one must make the necessary repairs. To keep the blood red and healthy, the teeth and bones strong, the circulation and digestion properly balanced, foods must be used which contain certain minerals. To remove the waste left by the food that the body consumes, there will be need of bulky foods which sweep the waste along as they pass through the intestines. And to insure growth and development, and protection against certain diseases foods must be used which contain substances called vitamins".

#### Fuel needs:-

Those who do hard physical work need more fuel foods than those who have employment which keeps them scated all day. When more fuel food is



taken into the body than is needed the surplus is stored up in the form of fat. The following table gives a list of some fuel foods:-

17		
STARCHES	SUGARS	FATS
Bread	Sugar	Butter
Crackers	Molasses	Cream
Cereals	Honey	Lard and other animal fats
Tapioca	Dried fruits	Olive oil
Macaroni	Candy	Cottonseed oil & corn oil
Rice		Chocolate
Potatoes		11

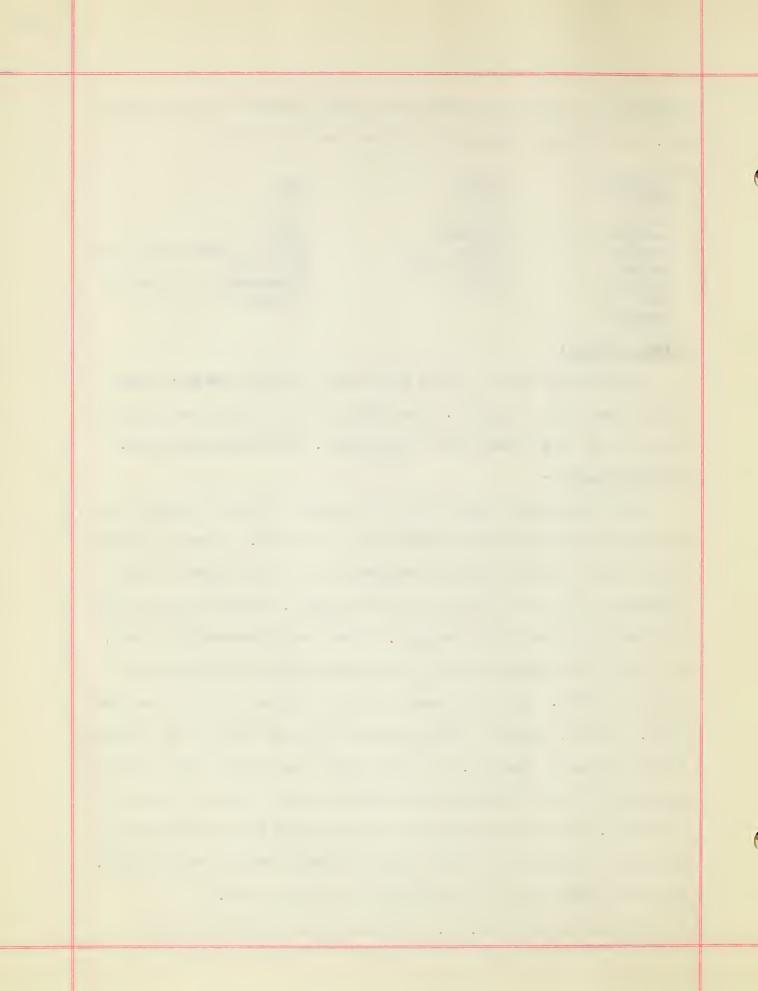
#### Tissue building:-

The wear and tear of living breaks down a certain amount of body tissue which must be replaced. Foods which contain proteins and mineral salts are the ones necessary for this purpose. They also supply fuel.

Regulating needs:-

Foods containing mineral salts are required for such processes as the beating of the heart and the circulation of the blood. If one is careful to eat foods containing calcium, phosphorous, and iron, there is little likelihood of the diet being short of other needs. Calcium is one of the most necessary minerals for the body. Without calcium-containing foods, the bones become porous and soft and the teeth poorly constructed and subject to decay. It is an essential building substance for the teeth and bones." Fruits, vegetables, whole grains, milk, and eggs are the principal foods which supply minerals. The first three also contain fibrous material which does not digest completely and serves to carry off waste through the intestines. Water helps to carry off waste through the skin and kidneys, and holds in solution in the body various elements derived from our food. One should drink from six to eight glasses of water a day."

35 - Metropolitan Life Ins. Co. - The Family Food Supply (Pamphlet)



#### Vitamins:-

"Nobody knows the chemical nature of vitemins, but that need not trouble us seriously. Nobody knows the nature of electricity, but we employ it to light our rooms, draw our trains, activate our radios, etc. we know where to find it and how to use it."

"About all we need to know about vitamins is that they are found in connection with the processes of life in plants and animals, that they are more or less completely destroyed by whatever destroys those life 36 processes." The following table contains a list of some vitamines with their use and source.

#### Vitamin A

#### Use

- 1. Produces growth and vigor.
- 2. Lessens danger of diseases of the eye, ear, nose, throat, kidneys, and skin.
- 3. Aids in tooth and bone development.
- 4. Helps digestion

#### General Source

Dutter
Cream
Whole milk
Cheese
Egg (yoke)
Liver and kidneys
Carrots & green vegetables

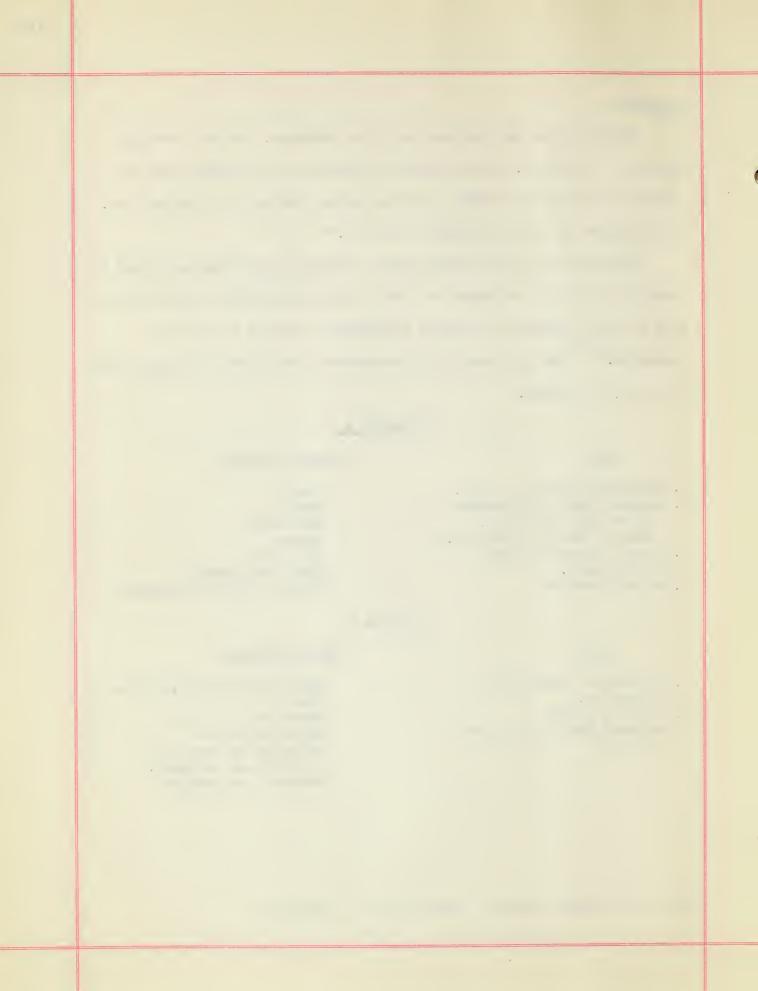
#### Vitamin B

#### Use

- 1. Stimulates appetite and digestion.
- 2. Promotes growth
- 5. Prevents beri beri (nerve disease)

#### General Source

Whole grain, breads, cereals
Milk
Dried peas and beans
Green vegetables
Roots and tubers like
carrots and potatoes.
Tomatoes and oranges



#### Vitamin C

#### Use

#### General Source

- 1. Promotes good tooth and bone development.
- 2. Protects body against tooth decay and gum disease.
- 3. Helps protect against so-called rheumatism.
- 4. Helps protect against irritability and fatigue in children.

Oranges
Tomatoes (cooked or raw)
Leafy vegetables
Cabbage (raw)
Pineapple

#### Vitamin D

#### Use

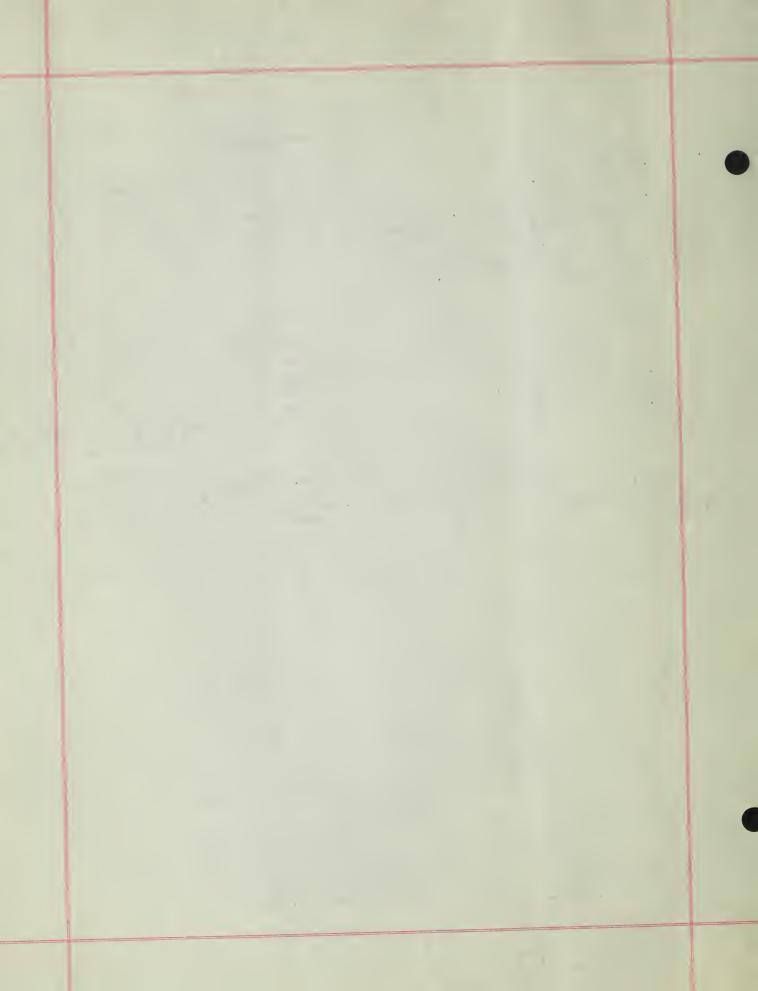
#### General Source

- 1. Promotes good tooth and bone development.
- 2. Helps prevent rickets

Egg (yoke)
Whole milk
Cod liver oil
Sunlight

37

The following page contains a chart which shows how to choose and use the foods that the body needs every day.



# H MEAT PIE

½ cup rice, uncooked 4 cups or a large can tomatoes 3 tablespoons fat

epper to taste

Amount Needed Every Day

**FOODS** 

i and the rice. melted fat. nd fry until light brown. toes to mixture and let simmer

vings.

#### **BEAN STEW**

Choose From These

2 tablespoons flour 2 tablespoons water 1 onion, chopped Salt and pepper to taste

t; drain. until tender. to the beans.

lour is cooked.

#### Ways of Using These Foods

#### JTE CABBAGE

3 tablespoons flour

Salt bage tter Pepper

and pepper, stirring constantly. make a smooth paste.

#### RICE PUDDING

1/2 teaspoon salt 1 tablespoon butter

# TO P

# Thes need in





A quart of milk, t vegetable or canne

> the wh  $\frac{1}{2}$  the  $\frac{1}{2}$  the more th vitamir

For the other half fruit, meat or mea

> BETH ISRAI BOSTON D

BOSTON H

# HOW TO CHOOSE AND USE THE FOODS THAT THE BODY NEEDS EVERY DAY

	1	1								
FOODS	MILK	CEREALS	BREADS	VEGETABLES		FRUIT	PROTEIN FOODS		FATS	SWEETS
Amount Needed Every Day	1 quart daily for a child  1 pint daily for an adult	A whole grain cereal at least once a day. Use refined cereal occasionally, if desired.	Whole grain bread at every meal.	Two or more daily, one of these raw or a leafy vegetable.		Two or more daily. One should be an orange or a tomato (fresh or canned)	Meat or fish once a day is desirable, with		3 level teaspoons of butter daily Of other fats 3 level teaspoons for the child 5 level teaspoons for the adult daily	of sugar daily 1/2 cup molasses every week
Choose From These		whole Grain brown rice cracked wheat Grapenuts Pettijohn Ralston rolled oats Shredded Wheat Wheatena whole corn meal  REFINED polished rice spaghetti macaroni noodles Farina crackers	whole GRAIN graham oatmeal rye whole wheat whole grain crackers	beet greens Brussels sprouts cabbage chard dandelion greens lettuce spinach  YELLOW carrots parsnips squash sweet potato turnip yellow beans yellow corn	asparagus beans string beans Lima beans beets cauliflower celery corn egg plant green peas kohlrabi okra onion radish potato	FRESH OR CANNED orange grapefruit tomato apple banana blackberries blueberries peach pear rhubarb strawberries  DRIED apricots dates prunes raisins peaches apples	ANIMAL For the seed of the see	ult)	butter bacon lard peanut butter salt pork vegetable fats vegetable oils other animal fats	brown sugar molasses white sugar honey jelly syrup preserves
Ways of Using These Foods	As a drink In cocoa Over cereals In vegetable soup In vegetable or fish chowder In cream sauce for vegetables In custard In pudding With some fruits, as banana and baked apple	As cereal In soup In pudding Macaroni or spaghetti served with tomato and cheese sauce Rice served with tomato sauce With dried fruit, as prunes	In milk toast For sandwiches of cheese vegetables meat Spread with cheese and tomato In puddings bread pudding apple pudding Toast and serve with to- mato and cheese sauce Serve with fruit sauce or molasses	over cooked rice Baked potato and cole slaw Scalloped cabbage or onion, potato with cream and cheese sauce In soups potato, tomato, carrot, onion, spinach, pea or		Fresh Stewed Baked Canned Preserved With cereals In puddings In salads	In vegetable stew Cooked with macaroni spaghetti rice	Serve eggs In custard In cream sauce over vegetables Serve beans Baked with tomato In soups with corn and milk	Serve butter In cooked vegetables In puddings On bread Serve oil With salads and vegetables Use other fats In cooking	Use molasses In gingerbread In ginger cookies In baked beans Spread over whole grain bread With cereal Use sugar In cooking or sparingly on foods

#### THE WAY TO PLAN MEALS\*

Breakfast { bread and butter milk for children coffee or tea for the adult

\*See above "Ways of Using These Foods"

Lunch or Supper a vegetable bread and butter simple dessert or fruit milk for children

# RECIPES

#### STUFFED FLANK STEAK

1½ lbs. flank steak
3 cups bread crumbs
1 tablespoon minced onion
1 tablespoon fat
Salt and pepper to taste
Any seasoning desired

Water, enough to make the mixture stick together

Mix bread crumbs, onion, fat, seasoning and water to make stuffing.

Spread the stuffing on the steak.

Roll and tie securely.

Cook as a pot-roast or in a covered dish in the oven for two to three hours.

One cup tomatoes may be used to baste meat while cooking. Serves eight.

### MINESTRONE

#### (Meatless Soup)

1 pint pea beans
1 large carrot
1 cup parsley, chopped
2 slices bacon or salt pork
5 stalks celery
1 large onion
2 can tomatoes
1 cup parsley, chopped
2 slices bacon or salt pork
1 cup macaroni, cooked
Salt and pepper to taste

Soak the beans over night.

In the morning drain and add 6 quarts of fresh cold water. When it boils, add the vegetables and the fat meat chopped very fine and cook slowly 4 hours.

Season with salt and pepper.

Add macaroni and let simmer 15 minutes before serving. Other vegetables than those named may be used.

This makes a very hearty dish.

Small bits of left-over meat may be added to the soup if desired. Serves twelve.

#### CHEESE AND POTATO SCALLOP

1½ lbs. potatoes
1 cup grated cheese
2 onions sliced
1½ cups hot milk
2 onions sliced
1½ teaspoon salt
1¼ teaspoon pepper

Pare and slice potatoes thin.

Let soak in water to cover one hour and drain.

Sprinkle the bottom of the dish with potatoes, then cheese, then onions and, last, bread crumbs.

Heat milk and fat together.

Add salt, pepper to milk.

Pour all over potatoes.

Bake 45 minutes or until potatoes are tender.

Serves six.

#### MACARONI MEAT PIE

3/4 lb. hamburg steak
2 onions, chopped
4 cups or a large can tomatoes
2 cups macaroni, uncooked
Salt and pepper to taste

Cook and drain the macaroni and the rice.

Brown the chopped onion in melted fat.

Add the meat to the onion and fry until light brown.

Add rice, macaroni and tomatoes to mixture and let simmer

for 10 minutes.
This furnishes ten liberal servings.

#### KIDNEY BEAN STEW

1½ cups dried kidney or other beans 2 tablespoons flour 2 tablespoons water 1 onion, chopped 5alt and pepper to taste

Pick over and wash beans.
Soak in cold water over night; drain.
Cook in boiling salted water until tender.
Add rice, onion and tomato to the beans.
Cook until rice is tender.
Make paste of flour and water.
Add to staw and boil until flour is cooked.

Add to stew and boil until flour is cooked. Serves six.

#### FIVE MINUTE CABBAGE

3 cups milk
1½ quarts shredded cabbage
3 tablespoons melted butter
3 tablespoons flour
Salt
Pepper

Heat milk.

Cook cabbage in it for 2 minutes.

Melt fat, add flour and salt and pepper, stirring constantly, and enough of hot milk to make a smooth paste.

Combine all together.

Combine an tog

Serves ten.

#### **MOLASSES RICE PUDDING**

4 cups milk

½ teaspoon salt

½ cup rice

1 tablespoon butter

½ cup molasses

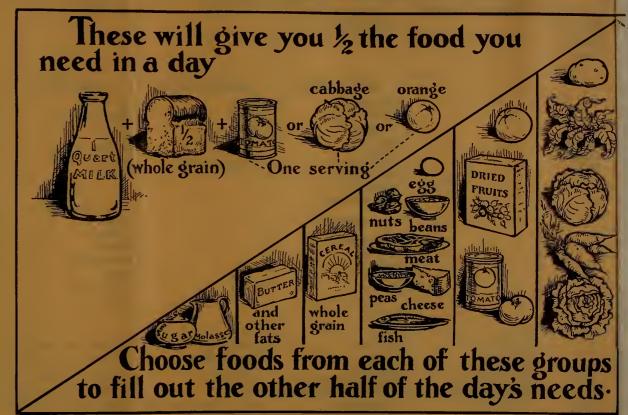
Wash rice.

Mix, and bake 30 minutes. Serves six.

New England Dairy and Food Council, Boston

# FEED YOUR BODY TO PROTECT YOUR HEALTH

First Leaflet of the Series



A quart of milk, together with about 10 slices of whole grain bread and a serving of a raw vegetable or canned tomato or an orange, will give to your body

the whole day's need of calcium for bones and teeth; 1/2 the day's need of protein for growth, muscle and repair; 1/2 the day's need of iron for the blood; more than 1/2 the day's need of energy for work and play; vitamins for growth and vigor.

For the other half of the day's needs, use a food from each of the various groups—vegetables, fruit, meat or meat substitutes, cereal, fats and sweets.

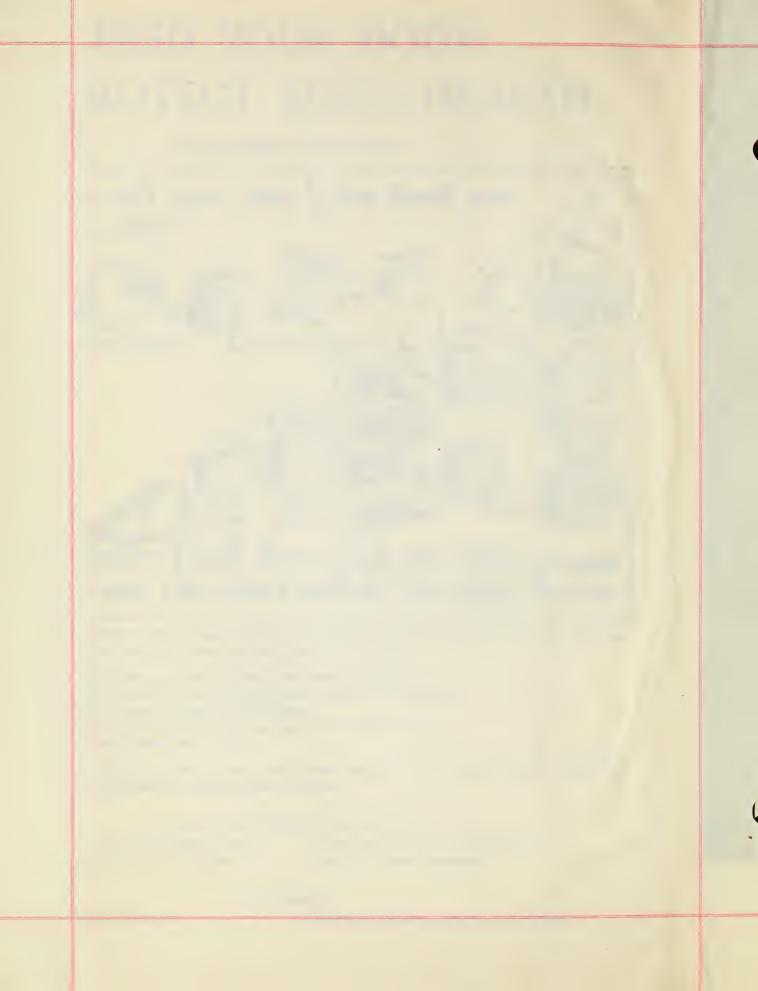
Prepared by the Nutrition Services of the

Beth Israel Hospital Food Clinic Boston Dispensary Food Clinic Community Health Association Forsyth Dental Infirmary

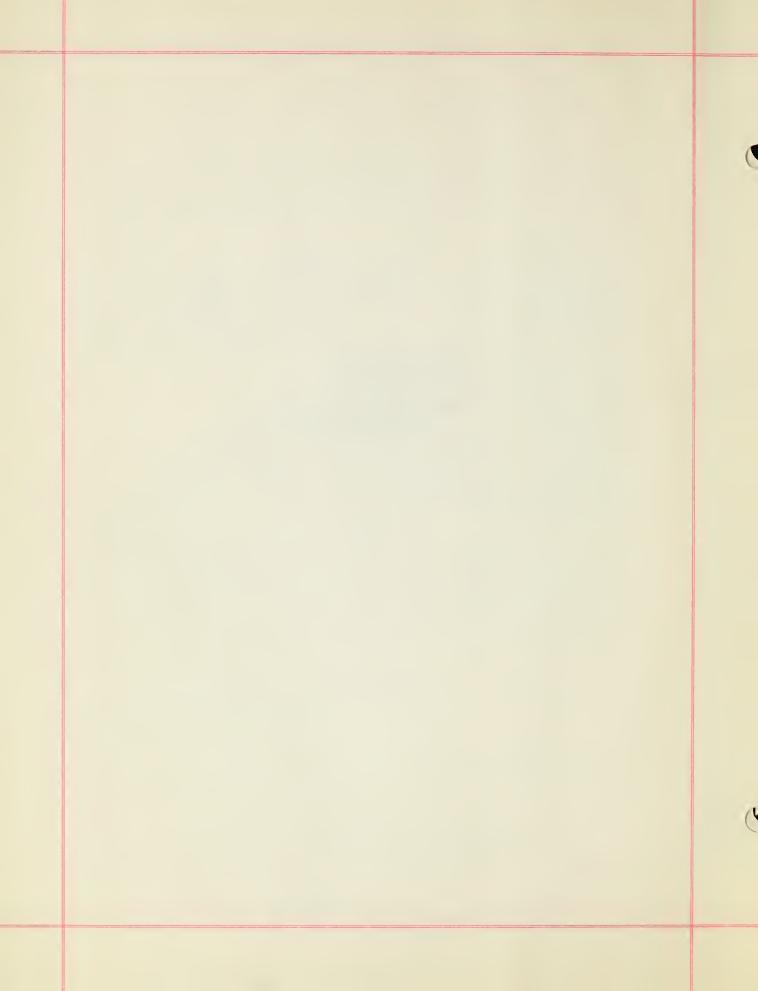
Distributed by

BOSTON HEALTH LEAGUE

BOSTON COUNCIL OF SOCIAL AGENCIES



APPENDIX I BIBLIOGRAPHY



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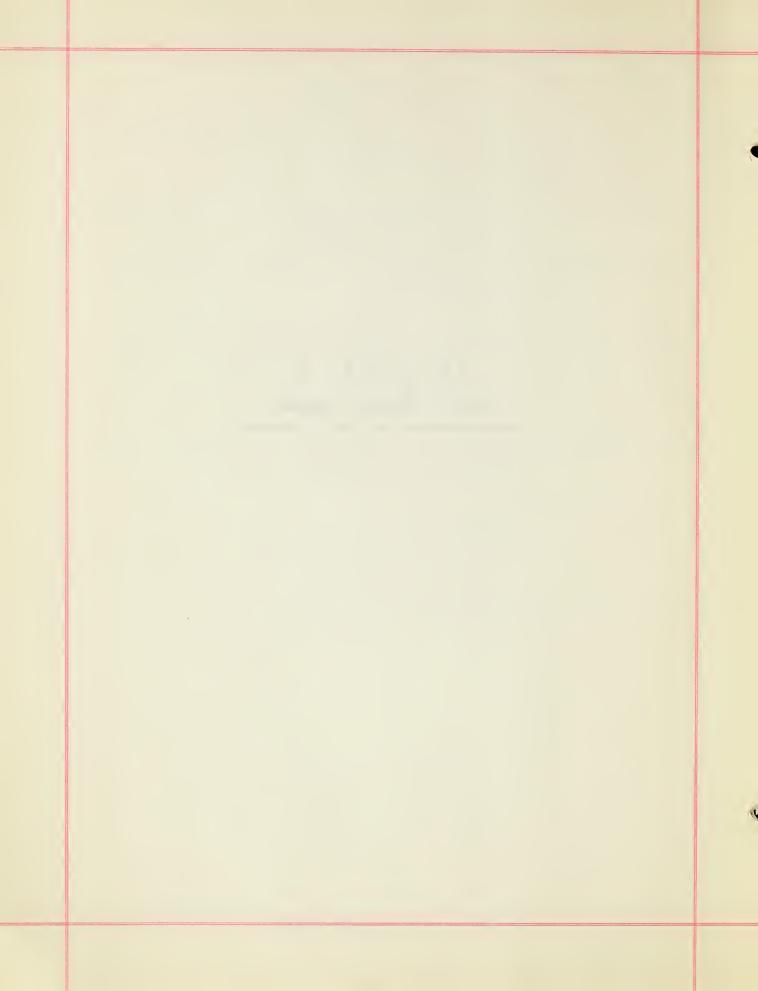
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APPENDIX II

KEY TO SOURCE OF DIAGRAMS



## KEY TO SOURCE OF DIAGRAMS AND ILLUSTRATIONS

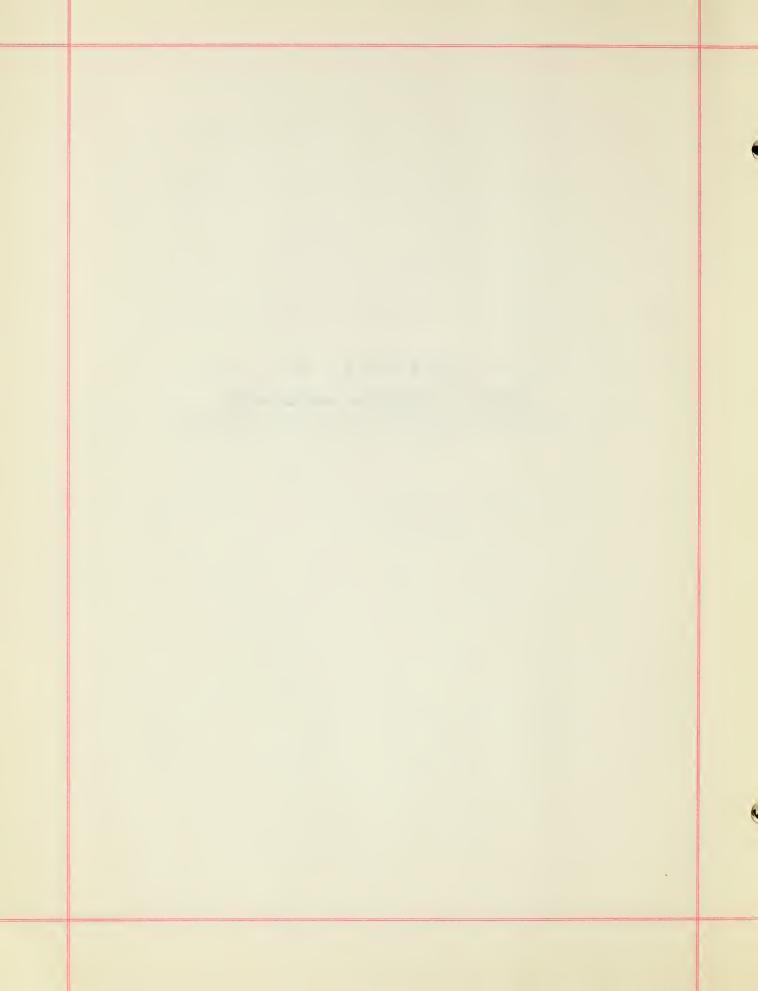
- Figure 1. Phelps, R.W. and Lake, F.W. Petroleum Engineering
  Page 148. (2nd Ed. 1927)
- Figure 2. Gray, C.W., Sandifur, C.W. & Hanna, H.J. Fundamentals of Chemistry (3rd Ed. 1929) Page 480.
- Figure 3. Campbell, Andrew Petroleum Refining (2nd Ed. 1922)
  Page 122.
- Figure 4. Campbell, Andrew Petroleum Refining (2nd Ed. 1922)
  Facing Page 61.
- Figure 5. Campbell, Andrew Petroleum Refining (2nd Ed. 1922)
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- Figure 7. Stansfield, E. and Carter, F.E. Products and By-Products of Coal. Canada Department of Mines. Printed by Government Printing Dureau, Ottawa, Canada.

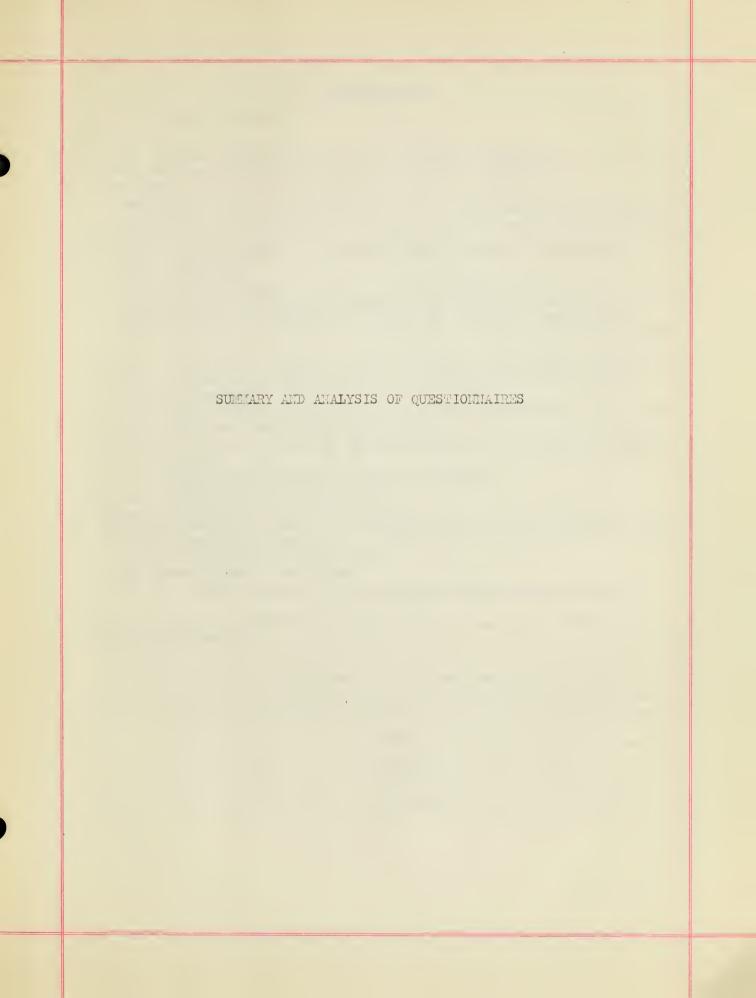
  Page 33.
- Figure 8. Lowy, Alexander and Harrow Benjamin Introduction to Organic Chemistry.

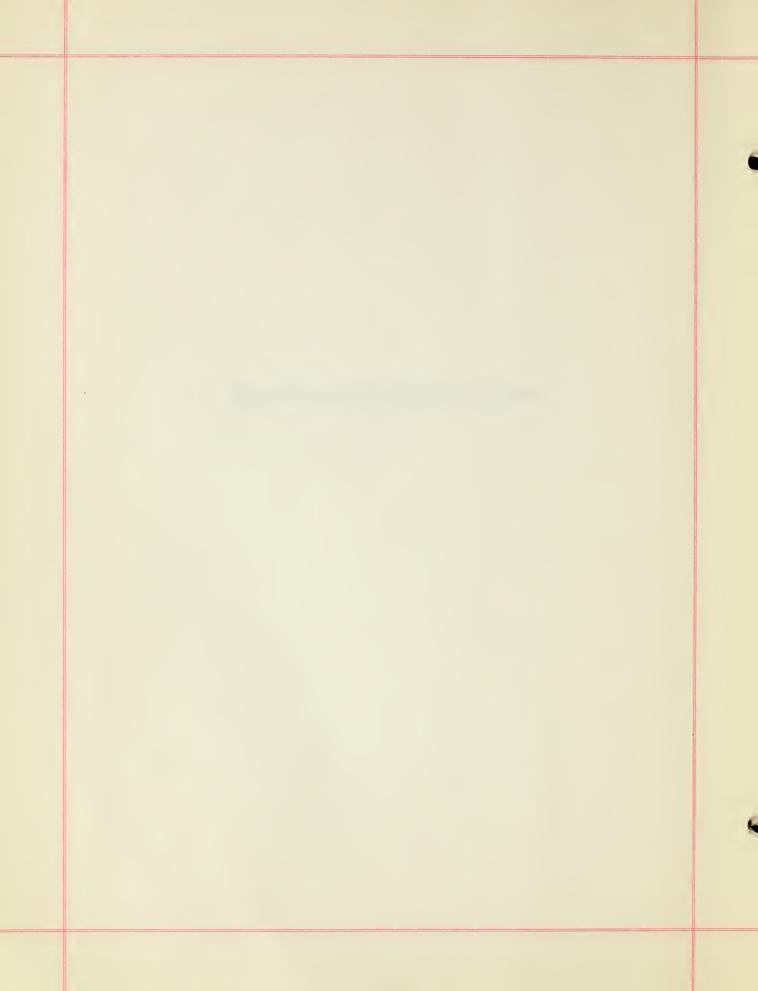
  John Wiley & Sons Inc. 1924. Page 198.
- Figure 9. "Facing Page 57
- Figure 10. "Facing Page 58
- Figure 11. " Facing Page 74
- Figure 12. " Facing Page 85
- Figure 13. " Facing Page 78
- Figure 14. Williams, J. G. Textiles on Test. Page 11.
- Figure 15. Keit, T. E. The Chemistry of Farm Practice. Page 37.

# APPENDIX III

SUMMARY AND ANALYSIS OF QUESTIONNAIRES

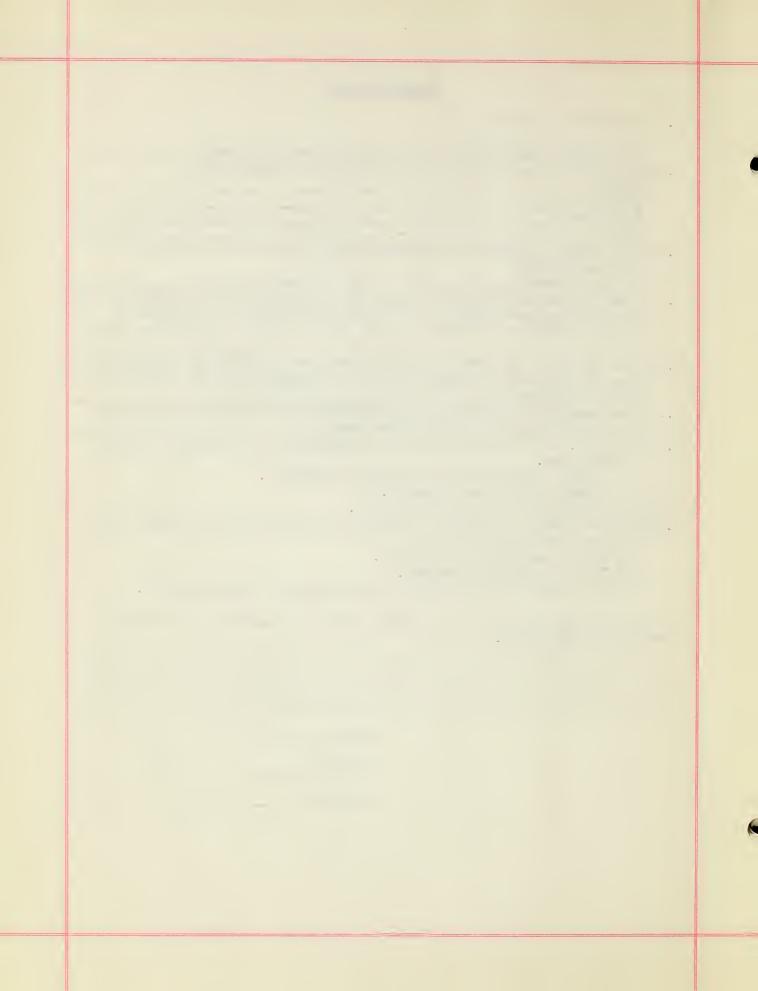






# QUESTIONNAIRE

1. Have you had a course in -
(a) General Chemistry? (b) Organic Chemistry?
2. What Text-book do you use in your teaching of Chemistry?
Title:-
Author: Publisher:
Date:
3. Do you teach the chapter in Organic Chemistry "as it is presented in
your text-book"?
(a) As a whole? (b) In part?
4. If the student is going to college, do you think that the purpose of the "organic chapter" should be - to give the student a foundation in
Organic Chemistry on which to build when he takes up the study again?
Of South Original of Market of Souther William To Course of Street of South Constitution
5. Do you consider the material in your text-book, adequately classified to
give the student a foundation for the continuance of his study of
Organic Chemistry? 6. Do you consider the material in your text-book descriptive enough for
the student who isn't going to college?
7. Mark "a, b, or c" in order of their importance to the organic chapter
in Chemistry.
Good classification of organic compounds.
Good descriptive material.  Abundant use of illustrations.
8. Would you favor the removal of obsolete materials and the installation
of newer materials such as -
(a) Latest material on petroleum.
(b) Latest material on rubber.
(c) The catalytic process for the preparation of wood alcohol.
Write below any new material you think should be included in the chapter
on Organic Chemistry.
Name
School
Address

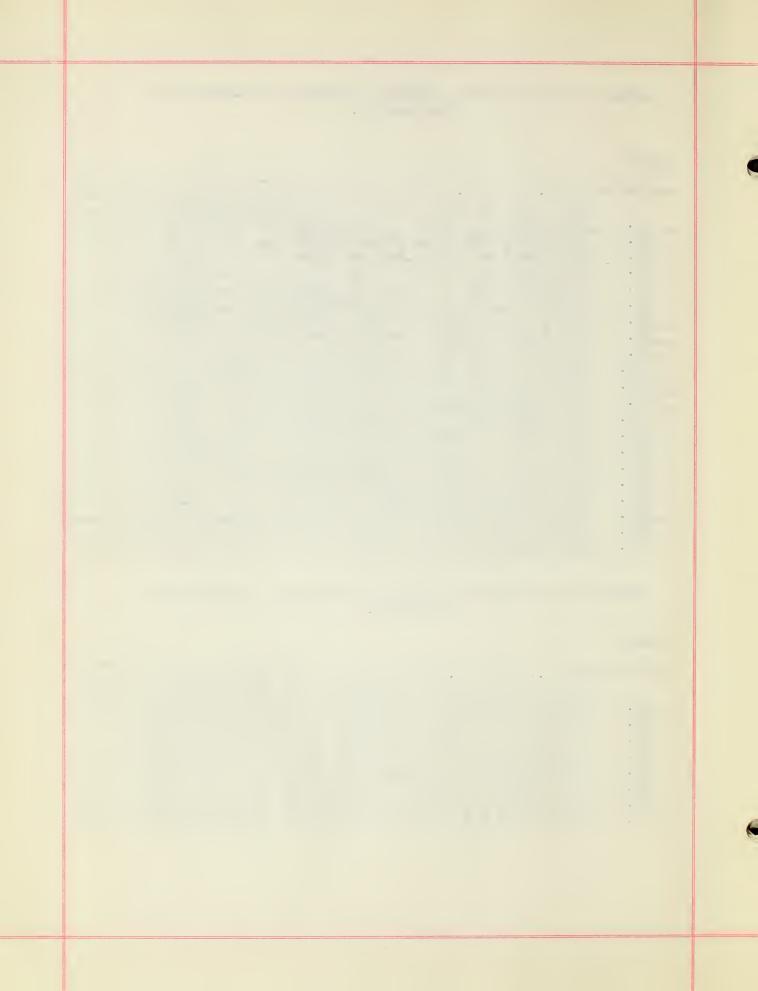


Summary of Questionnaires Returned by Teachers of Chemistry in High Schools.

Number												
of												
Questionnaire	1.		3.					7				
	a	Ъ	a	Ъ	4	5	6	(1)	(2)	(3)	8	
#1·	yes	yes	?	yes		no	yes	2.	С	Ъ	yes	
#2.	yes	yes	yes	?	yes	yes	yes	a	ъ	С	?	
#3.	yes	no	no	yes	yes	no	yes	Ъ	a	_ C	yes	
#4.	yes	yes	no	?	no	no	no	a	С	ď	yes	
<i>#</i> 5	yes	yes	yes	?	no	no	yes	С	a	Ъ	yes	
7/F6 •	yes	?	yes	?	?	gres	yes	?	?	?	?	
#7 <b>.</b>	yes	?	no	yes	yes	no	yes	a	ъ	С	yes	
#8.	yes	yes	?	yes	no	no	yes	а	ď	С	yes	
#9.	yes	yes	yes	?	yes	yes	no	2,	Ъ	С	?	
#10.	yes	?	?	yes	no	no	no	ವಿ	ъ	С	yes	
#11 <b>.</b>	yes	no	yes	?	?	?	yes	a	ъ	С	yes	
#12.	yes	yes	no	yes	no	no	no	a	С	Ъ	yes	
#13.	yes	yes	yes	?	?	no	yes	Ъ	a	С	yes	
#14 <b>.</b>	yes	yes	?	yes	yes	no	no	С	a	Ъ	yes	
#15.	yes	no	no	yes	no	no	?	С	a	ъ	yes	
#16 <b>.</b>	yes	no	?	yes	no	no	yes	ъ	a.	С	?	
<i>#</i> 17.	yes	yes	yes	?	no	no	no	2	Ъ	С	yes	
#18 <b>.</b>	no	yes	no	yes	yes	yes	yes	а	Ъ	С	yes	
<i>#</i> 19.	yes	?	no	yes	no	?	yes	С	a	Ъ	yes	
#20 <b>.</b>	yes	no	?	?	no	no	?	?	?	?	?	
<i>柴</i> 21.	yes	yes	no	no	?	no	no	a	ъ	С	yes	

Summary of Questionnaires Returned by Writers of Textbooks in Chemistry.

Number												
of												
Questionnair	е	1	3.					7				
	a	Ъ	a	ъ	4	5	6	(1)	(2)	(3)	8	
<i>#</i> 1.	yes	no	yes	no	yes	yes	?	೭	ъ	С	?	
#2.	yes	no	no	yes	?	yes	?	С	Ö	a	yes	
#3.	yes	no	?	yes	yes	yes	yes	ъ	ಡಿ	С	?	
://4.	yes	yes	yes	?	yes	yes	yes	a	ъ	С	yes	
<i>∜</i> 5.	yes	yes	yes	?	yes	yes	yes	а	С	ъ	?	
:#6 •	yes	yes	no	yes	?	yes	yes	а	С	Ъ	yes	
://-7 .	yes	yes	yes	?	?	yes	yes	С	E.	Ъ	yes	
<i>;#</i> 8.	yes	yes	?	?	no	no	yes	a	ъ.	С	?	



The analysis of the questionnaires returned by textbook writers showed that the majority had the following opinions.

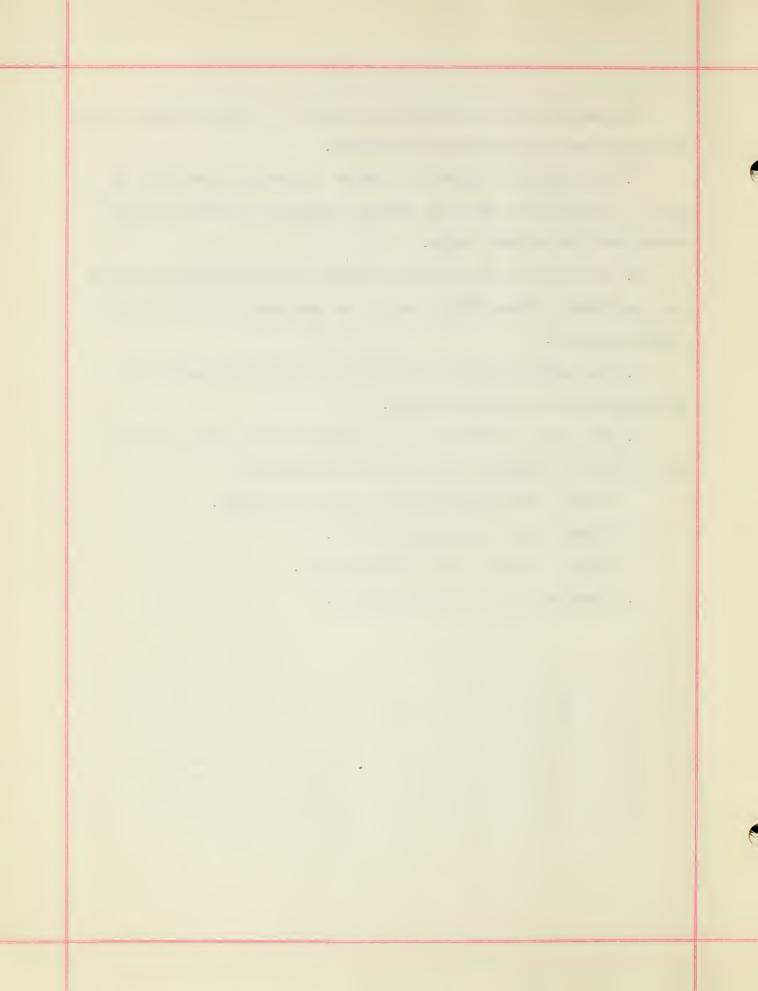
- 1. The purpose of the organic chapter in chemistry should be, to give the student who is going to college a foundation on which to build when he takes up the study again.
- 2. The materials in the textbooks used are adequately classified to give the student a proper foundation for the continuance of his study of organic chemistry.
- 3. The material in the textbook used is descriptive enough for students who are not going to college.
- 4. The order of importance of (1) classification, (2) descriptive material, and (3) abundant illustrations, is as follows:-

First - Good classification of organic compounds.

Second - Good descriptive material.

Third - Abundant use of illustrations.

5. Newer materials should be included.



The analysis of the questionnaires returned by teachers of chemistry in high schools showed that the majority had the following opinions.

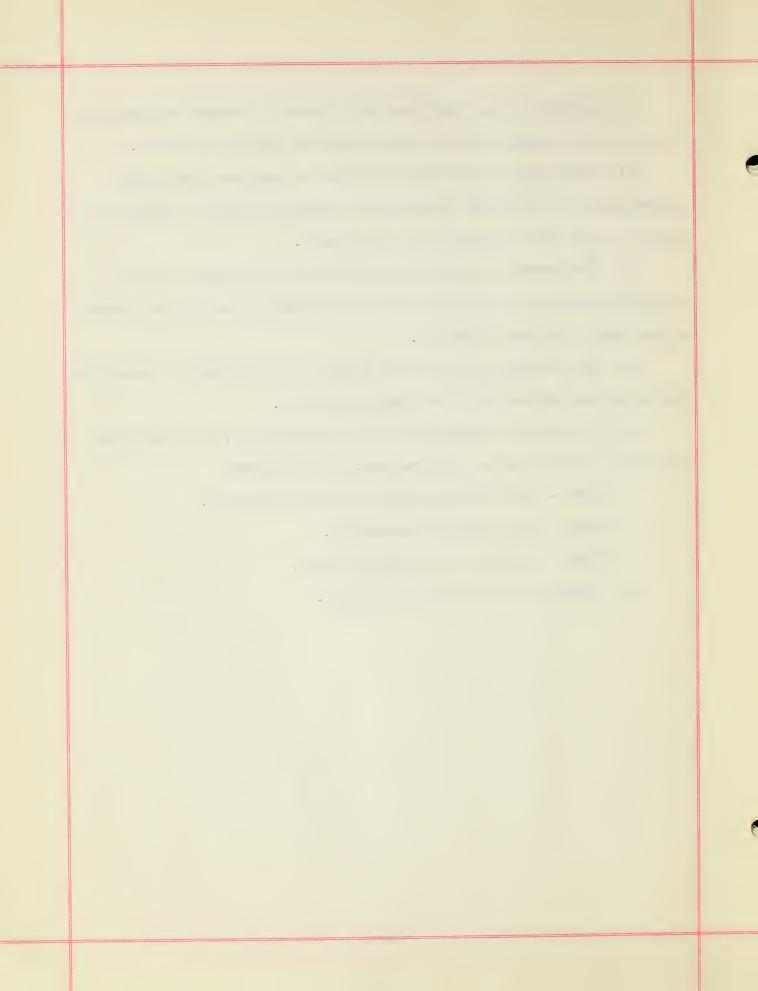
- (1) The purpose of the organic chapter in chemistry should <u>not</u> necessarily be, to give the student who is going to college a foundation on which to build when he takes up the study again.
- (2) The material in high school textbooks on the whole is <u>not</u> adequately classified to give the student a foundation for the continuance of his study of organic chemistry.
- (3) The material in high school textbooks on the whole is descriptive enough for the student who is not going to college.
- (4) The order of importance of (1) classification, (2) descriptive material, and (5) abundant illustrations, is as follows:

First - Good classification of organic compounds.

Second - Good descriptive material.

Third - Abundant use of illustrations.

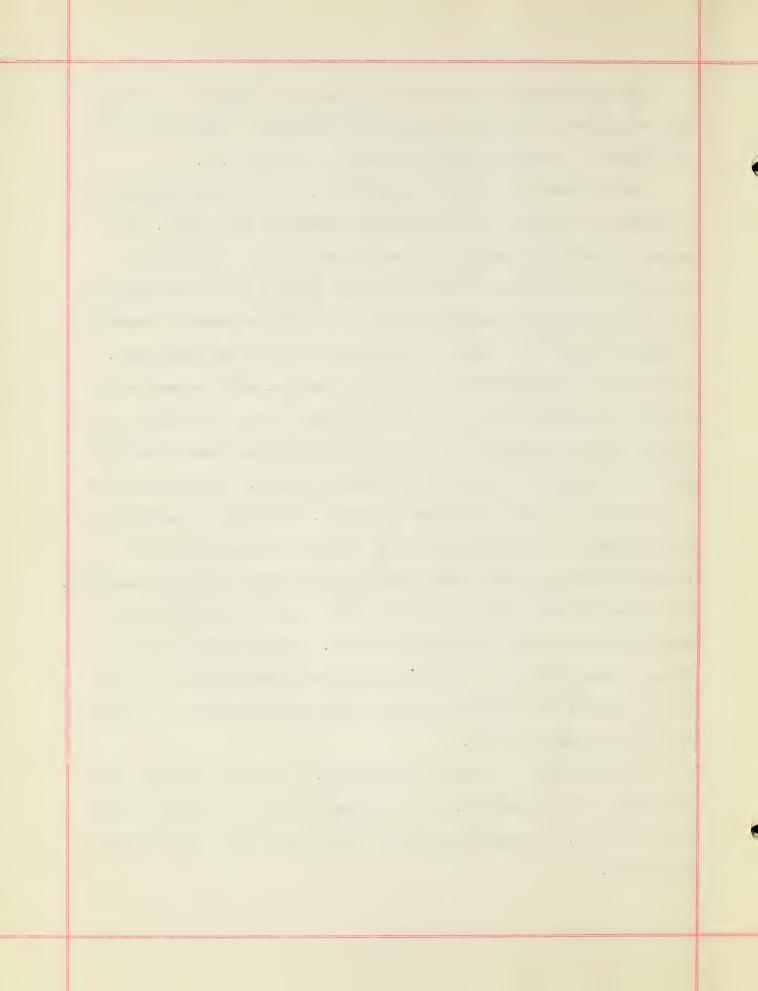
(5) Newer materials should be included.



The questionnaires show that the opinion of the teachers of chemistry who are writers of textbooks and that of the teachers of chemistry who are not writers of textbooks differs on question No. 4 and No. 5.

The difference in opinion on question No. 4 is very likely caused by a difference in types of classes which the teacher is instructing. The teacher of college preparatory students is very likely to answer this question from that point of view and have the opinion that - the purpose of the organic chapter in chemistry should be, to give the student a foundation in organic chemistry on which to build when he takes up the study again. The teacher of students who are not going to college, will, in most cases answer this question in the negative for, in their work, the purpose of the organic chapter in chemistry is to give the student some general knowledge which will help him in his life in an industrial world. This appears to me a logical reason for the difference of opinion. Of course, in explaining this difference, I have assumed that the teachers of chemistry who are textbook writers are most likely instructing the college preparatory students. This assumption seems plausible since the best qualified instructors are usually given to college preparatory students. In this thesis, which will follow, I have attempted to include enough material to satisfy the aims of both the teacher of college preparatory students and the teacher of students who are not going to college.

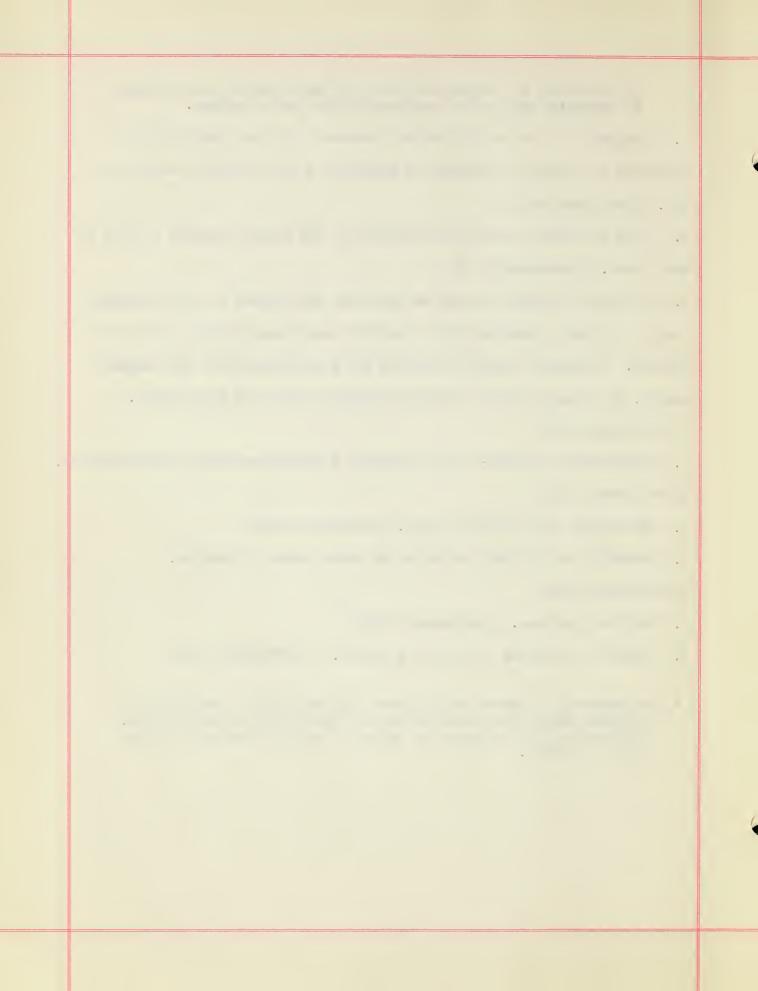
The difference of opinion on question No. 5 is easily understood then we consider that the teacher who is a textbook writer and uses his own book in his teaching, can hardly be expected to criticize a book that he himself has written.



The summary of suggestions made, for new material, by teachers of chemistry who are not textbook writers is as follows.

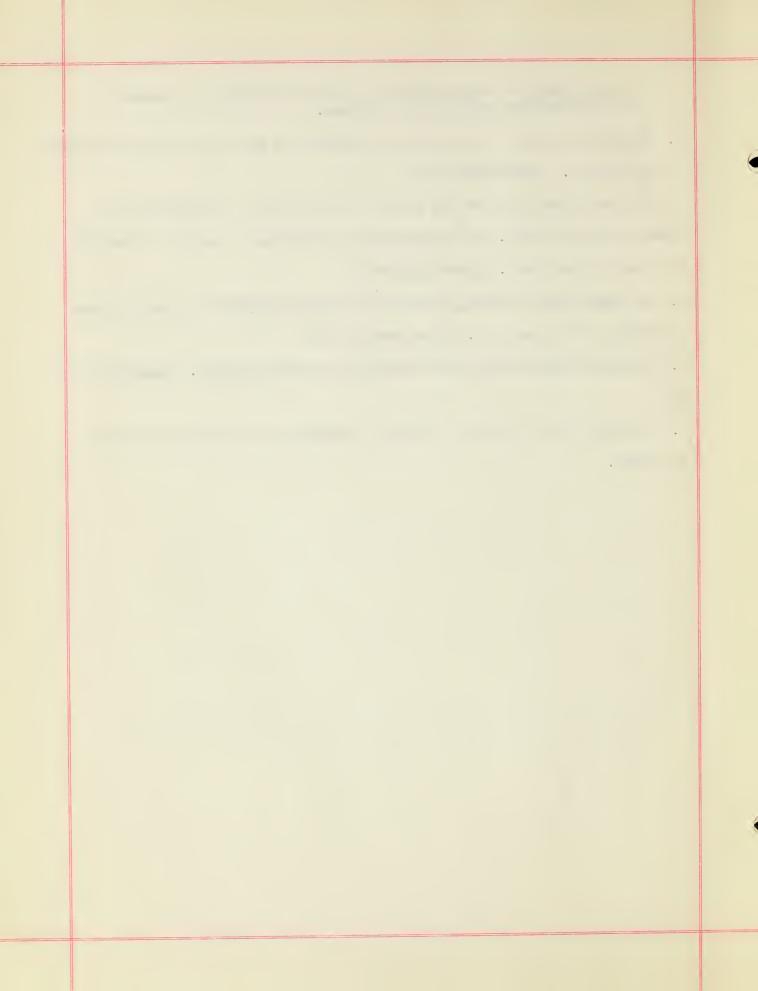
- 1. Paragraphs on the various organic processes for the manufacture of materials with which the student is familiar, such as rubber, petroleum, etc. (questionnaire #5)
- 2. Chart or diagram showing the relation of the several organic classes to each other. (questionnaire \*9)
- 3. The organic materials could be presented much better by a one semester course in organic chemistry with a textbook organized expressly for this purpose. If general organic chemistry was a prerequisite to this organic course, the student could be offered something very much worth while.

  (questionnaire #9)
- 4. Manufacture of rayon high explosives correct and easy classifications. (questionnaire #12)
- 5. \*Cellophane and synthetic sugar. (questionnaire #15)
- 6. Materials dealing with medicine for those taking up nursing. (questionnaire #14)
- 7. Coal tar products. (questionnaire #19)
- 8. Bakelite medicine coal tar products. (questionnaire #21)
  - \* The synthesis of sugars has not been included in this compilation, although suggested, on account of the complexity of this subject. The study of the synthesis of sugar is too far advanced for high school students.



The summary of suggestions made, for new material, by teachers who are textbook writers is as follows.

- 1. The organic chapter should give the student an idea of the classifications in the subject. (questionnaire #1)
- 2. If the fundamentals are not given, let's not call it chemistry, but a general science course. No student can say he has had a course in chemistry if it was in name only. (questionnaire #1)
- 3. You cannot give a thorough course in organic chemistry and teach general chemistry, all in one year. (questionnaire #1)
- 4. Too many illustrations teach nothing and are too complex. (questionnaire
- 5. New process for synthetic methanol, something on plastics and a little on rubber.



Index to questionnaires returned by teachers of chemistry who are not textbook writers.

## Questionnaire Number

- #1. H. C. Cambee, Phoenix High School, Phoenix, Arizona.
  - Book used:- Introductory Chemistry, by Neil Gordon.
  - Published by:- World Book Company
    Yonkers-on-Hudson, New York.
- #2. Henry M. Snyder, Head of Science Department, Wilmington High School, Wilmington, Delaware.
  - Book used:- First Principles of Chemistry by R. B. Brownlee, W. J. Hancock, J. E. Whitsit, R. W. Fuller, and M.D.Sohon.
  - Published by: Allyn and Bacon, New York City.
- #3. Theodore Sargent, Tuckahoe High School, Tuckahoe, N.Y.

  Book used: First Principles of Chemistry by R. B. Brownlee,
  W. J. Hancock, J. E. Whitsit, R. W. Fuller, and M.D.Sohon.
- A. G. Brown, Washington Senior High School, Cedar Rapids, Iowa.

  Book used:- First Book in Chemistry, by R. H. Bradbury.

  Published by D. Appleton and Company.
- #5. George H. Ridgway, Academy of Richmond County, Augusta, Georgia.

  Book used:- First Principles of Chemistry, by R. B. Brownlee,
  W. J. Hancock, J. E. Whitsit, R. W. Fuller and M.D.Sohon.

  Published by Allyn and Bacon, New York City.
- #6. S. H. Skinner, Redland High School, Redland, California.

  Book used: Practical Chemistry, by Black and Conant.

  Published by: The Macmillan Company, Boston, Mass.

# Questionnaire Number

- #. B. Simpson, Central High School, Syracuse, New York.

  Book used:- Not mentioned.
- #3. Grace Bagby, Flint Central High School, Flint, Mich.

  Book used:- First Principles of Chemistry by R. B. Brownlee,
  W. J. Hancock, J. E. Whitsit, R. W. Fuller, and M.D.Sohon.

  Published by:- Allyn and Bacon Co., New York City.
- #9. George M. Harvey, Edmunds High School, Burlington, Vt.

  Book used: General Chemistry, by R. B. Brownlee, W. J. Hancock,
  J. E. Whitsit, R. W. Fuller, and M.D. Sohon.
- #10. W. H. Coffin, Boise High School, Boise, Idaho.

  Book used:- First Principles of Chemistry by R. B. Brownlee,
  W. J. Hancock, J. E. Whitsit, R. W. Fuller, and M.D.Sohon.

  Published by:- Allyn and Bacon, New York City.
- Book used:- Chemistry and Its Uses by McPherson and Henderson.

  Published by:- Ginn and Company, Boston, Mass.
- #12. J. S. Shalk Jr., Sunset High School, Dallas, Texas.

  Book used: Chemistry and Its Uses by Irwin, Rivett, and Tatlock.

  Published by: Row Peterson and Company.
- Book used: Fundamentals of Chemistry, by C. W. Gray, C.W. Sandifur and H. J. Hanna.

  Published by: Houghton, Mifflin Company, New York City.

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## Questionnaire Number

- #14. D. G. Van Ormer, Kane High School, Kane, Pa.

  Book used:- Beginning Chemistry, by Fletcher, Smith, and Harrow.

  Published by:- American Book Company.
- #15. A. O. Herbert, Holyoke High School, Holyoke, Mass.

  Book used:- A First Book in Chemistry, by Robert H. Bradbury.

  Published by:- D. Appleton and Company.
- #16. H. W. Matzke, Senior High School, Ann Arbor, Hich.

  Book used: Modern Chemistry, by C. E. Dull.

  Published by: Henry Holt and Company.
- #17. H. W. Kline, Head of the Science Department, Jamestown, New York.

  Book used:- No book.
- Book used:- First Principles of Chemistry, by R. B. Brownlee,
  W. J. Hancock, J. E. Whitsit, R. W. Fuller and M.D.Sohon.

  (For college preparatory students) General Chemistry,
  by Mcpherson (for general students)
  - Published by: Allyn and Bacon, New York City, and Ginn & Co., respectively.
- #19. J. J. Millan Jr., Ludlow High School, Ludlow, Mass.

  Book used: Beginning Chemistry, by Fletcher, Smith and Harrow.

  Published by: The American Book Company.
- #20. Samuel C. Rosenthal, Portland High School, Portland, Me.

  Book used: No book used.

Index to questionnaires returned by teachers of chemistry who are textbook writers.

## Questionnaire Number

#1. C. W. Gray, Hollywood High School, Hollywood, California.

Book used: Fundamentals of Chemistry, by C. W. Gray, C.W. Sandifur and H. J. Hanna.

Published by: - Houghton Mifflin Company.

#2. C. H. Schmidt (answered for Mr. Whitsit) DeWitt Clinton High School, New York City.

Book used:- First Principles of Chemistry by R. B. Brownlee, W. J. Hancock, J. E. Whitsit, R. W. Fuller and M.D.Sohon.

Published by:- Allyn and Bacon, New York City.

#5. Raymond B. Brownlee, Stuyvesant High School, New York City.

Book used:- First Principles of Chemistry, by R. B. Brownlee, W. J. Hancock, J. E. Whitsit, R. W. Fuller and M.D.Sohon.

Published by: - Allyn and Bacon, New York City.

#4. C. W. Sandifur, North Hollywood High School, Hollywood, Cal.

Book used:- Fundamentals of Chemistry, by C. W. Gray, C.W. Sandifur and H. J. Hanna.

Published by: - Houghton Mifflin Co.

#5. Howard J. Hanna, Los Angeles High School, Los Angeles, Cal.

Book used:- Fundamentals of Chemistry, by C. W. Gray, C.W. Sandifur, and H. J. Hanna.

Published by Houghton, Mifflin Co.,

#6. Ernest L. Dinsmore, Boys High School, Brooklyn, N. Y.

Book used: - Chemistry for Secondary Schools, by E. L. Dinsmore.

Published by: - F. Ambrose Company.

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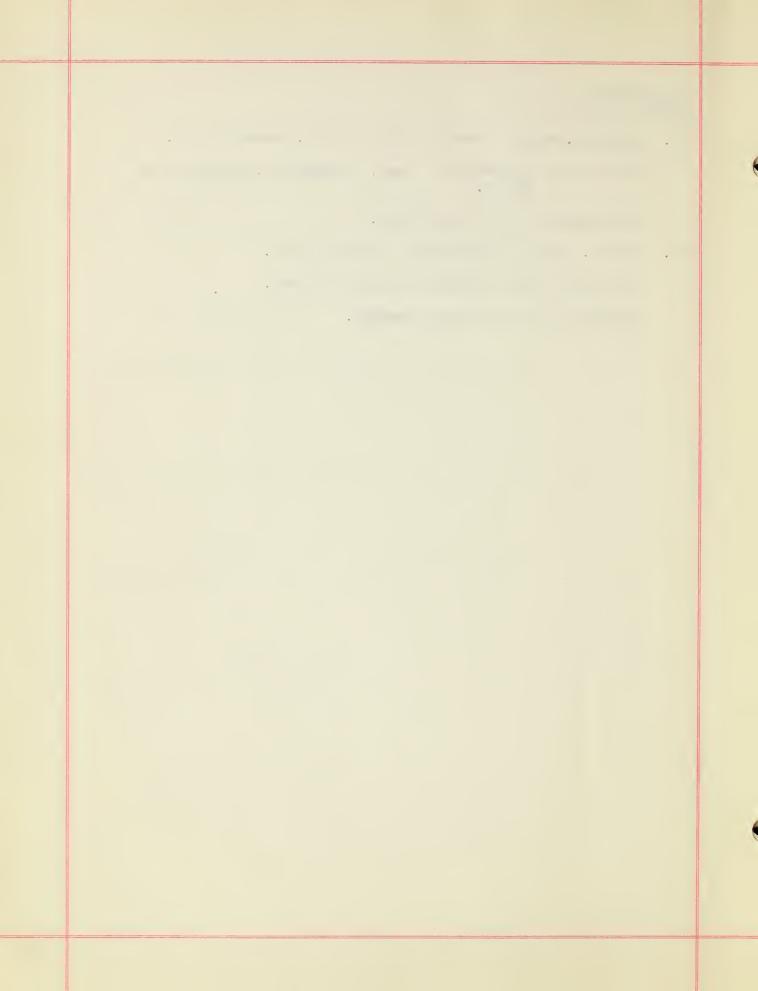
## Questionnaire Number

- #7. George W. Fowler, Board of Education Bldg. Syracuse, N. Y.

  Book used:- Chemistry for Today, by McPherson, Henderson, and
  Fowler.
  - Published by: Ginn and Company.
- #8. John C. Hessler, Knox College, Galesburg, Ill.

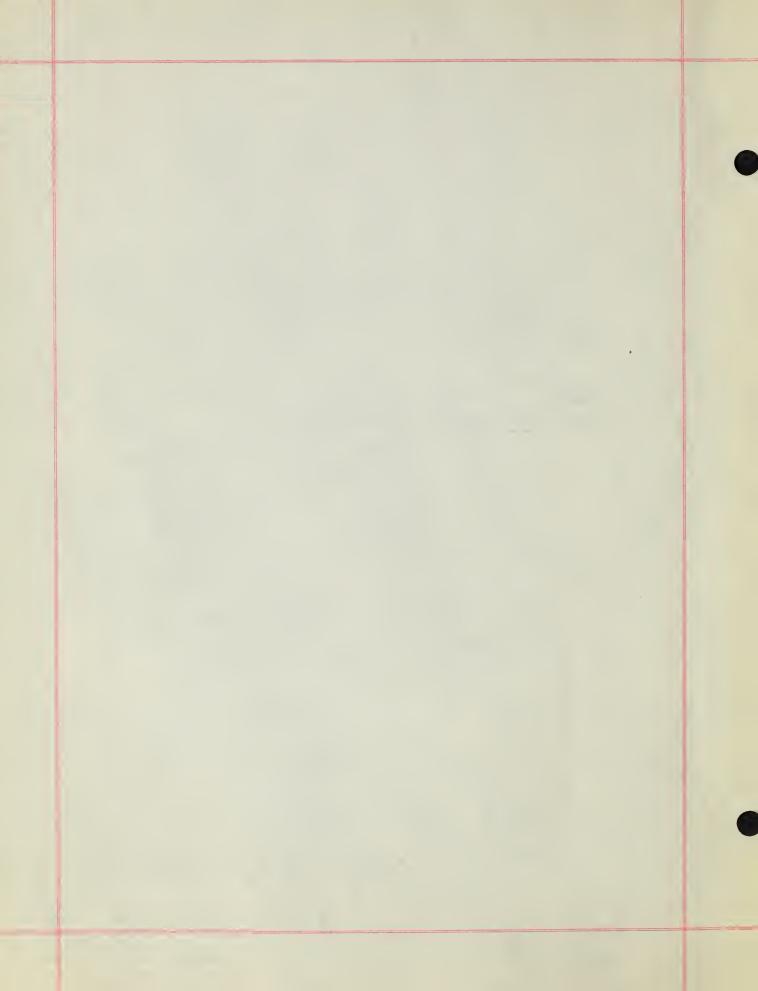
  Book used: Smith, Kendall College Chemistry.

  Published by: The Century Company.



APPENDIX IV

NEW MATERIALS INTRODUCED



## NEW MATERIALS INTRODUCED

- 1. Catalytic process for making methyl alcohol from (a) carbon monoxide and hydrogen (b) carbon dioxide and hydrogen.
- 2. Manufacture of butyl alcohol by the bacterial fermentation of corn.
- 3. Manufacture of "celotex" a substitute for lumber from "bagasse".
- 4. Manufacture of synthetic rubber.
- 5. Manufacture of glycerine by the hydrolysis of fats.
- 6. Marcotics, anaesthetics and purgatives. (chemistry of medicine)
- 7. Alcohol from sawdust.
- 8. Manufacture of nitro-cellulose, nitro-glycerine & T.N.T.
- 10. Plastics: bakelite, artificial ivory, cellophane, and artificial hair.
- 11. Chart showing the relationship between classes of organic compounds.
- 12. Production of rubber.
- 13. Cosmetics.

Date Due

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Demco 29	3-5			



Thesis Quallins, G.A. 1933

Quallins, George Andrew
The reorganization of the organic chapter in chemistry for secondary school text-books.

